APPLICATION AND INTEGRATION OF RUTHENIUM CATALYSTS FOR WATER

TREATMENT AND RESOURCE RECOVERY

by

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ABSTRACT

Water contaminants in oxidized form can be preferably removed or transformed to less harmful species by chemical or biological reduction. Hydrogenation metal-catalyzed reduction has emerged as a promising treatment technology for oxidized pollutants (e.g., oxyanions, halo- and nitro-organics). To date, Pd-based catalysts have received significant attention and demonstrate good activity and stability in reducing a number of contaminants relevant to drinking water or groundwater, but the deployment of catalytic reduction systems remains limited, in large part, by the high cost and volatile market price of this metal. The narrow focus on Pd-based materials also hinders the advancement of catalytic reduction technology because other hydrogenation metals are being overlooked which may have exhibited higher activity for specific contaminants. In addition, demonstrating catalytic activity with multiple metals can reduce uncertainty in the cost of the technology by allowing for metal substitution during market price spikes. Thus, it is necessary to expand catalyst "toolbox" for the water treatment applications and to integrate catalysts with other technologies (e.g., separations processes) to advance the development of practical water catalysis technologies.

To develop alternative hydrogenation metal catalysts for water purification, several supported platinum group metals catalysts were assessed with a suite of representative oxyanion pollutants. Rh, Ru, Pt and Ir were found to exhibit higher activity, wider substrate selectivity or variable pH dependence in comparison to Pd. A detailed investigation, coupling experiments with computational work, was then conducted to identify mechanisms controlling nitrate and nitrite reduction by supported Ru catalysts. Pseudo-first-order rate constants and turnover frequencies were determined for carbon- and alumina-supported Ru, and this work demonstrated

Ru's high activity for hydrogenation of nitrate at ambient temperature and H_2 pressure. Pretreatment of the catalysts was found to enhance nitrate reduction activity by removing catalyst surface contaminants and exposing highly reducible surface Ru oxides. Ru reduces nitrate selectively to ammonia and nitrite to a mixture of ammonia and N_2, with the product distribution determined by the initial aqueous nitrite concentrations. Experimental observation and Density Functional Theory calculations together support a reaction mechanism wherein sequential hydrogenation of nitrate to nitrite and NO is followed by parallel pathways involving the adsorbed NO that lead to ammonia and N_2.

The activity of supported Ru catalysts was further evaluated for reducing N-nitrosamines, including the toxic disinfection byproduct N-nitrosodimethylamine (NDMA) and other organic water contaminants. Using NDMA as a representative contaminant, commercial Ru/Al_2O_3 catalyst showed high activity with an initial turnover frequency (TOF_0) of 58.0 ± 7.0 h^{-1}. A second Ru/Al_2O_3 catalyst was synthesized using an incipient wetness impregnation technique, and this catalyst exhibited higher initial pseudo-first-order rate constant than the commercial catalyst due to higher dispersion of Ru nanoparticles on the catalyst support. NDMA was reduced to dimethylamine (DMA) and ammonia end-products, and a small amount of 1,1-dimethylhydrazine (UDMH) was detected as a transient intermediate. Experiments with a mixture of five N-nitrosamines spiked into tap water (1 µg L^{-1} each) demonstrated that Ru catalysts are very effective in reducing a range of N-nitrosamine structures at environmentally relevant concentrations. These results encourage the further development of Ru catalysts as part of the water purification and remediation toolbox.

Supported Ru catalyst was then integrated into a hybrid catalytic hydrogenation/membrane distillation process to improve nitrate-contaminated ion exchange

waste brine management and recover valuable nitrogen resources. The ability of a commercial Ru/C catalyst to reduce concentrated nitrate was demonstrated in a semi-batch reactor under typical waste brine conditions. Nitrate hydrogenation exhibited zero-order kinetics, attributed to saturation of available surface reaction sites, and the apparent rate constant was influenced by both solution chemistry and reaction temperature. The resulting ammonia product was efficiently recovered using membrane distillation. At low temperatures (<35 °C), solution pH showed significant impact on ammonia mass transfer coefficient by controlling the free ammonia species fraction. Ammonia recovery efficiency was not affected by salt levels in the brine, indicating the feasibility of membrane distillation for recovering ammonia from waste ion exchange brine. The hybrid catalytic hydrogenation/membrane distillation process was also applied to a real ion exchange waste brine and demonstrated high nitrate hydrogenation and ammonia recovery efficiency. These findings provide alternative catalyst for catalytic treatment of ion exchange waste brine and design option of efficient, low footprint system for nitrogen resource recovery from waste ion exchange brines.

In addition, the efforts of catalyst and process development were extended to the field of bio-renewable energy. Leveraging fuel property predictive models, a non-cyclic branched C_{14} hydrocarbon (5-ethyl-4-propylnonane) was identified to be a potential target molecule for renewable diesel applications. This target molecule is accessible from butyric acid through sequential catalytic reactions of acid ketonization, ketone condensation, and hydrodeoxygenation. Catalytic activity, product selectivity, and catalyst stability for individual conversion step were first evaluated, followed by demonstration of hydrocarbon blendstock production from butyric acid through integrated conversion process scheme. Experimental fuel property testing of the conversion product validated its suitability for use as diesel blendstock.

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CHAPTER 1

INTRODUCTION AND MAIN OBJECTIVES

1.1 Background

1.1.1 Catalytic treatment of oxyanion water contaminants

Toxic oxyanions, such as nitrate (NO_3^-), nitrite (NO_2^-), bromate (BrO_3^-), chlorate (ClO_3^-), and perchlorate (ClO_4^-), are common drinking water contaminants. Nitrate contamination of surface and groundwater has gradually increased due to excess fertilizer applications, poor disposal of animal waste, and release of incompletely treated industrial and domestic wastewater.[1-3] The presence of bromate is mainly due to the ozonation of bromide-containing source waters, and bromide has various natural and anthropogenic sources, such as seawater intrusion, pesticide run-off, industrial wastes and impurities from road de-icing salts.[4] Perchlorate contamination is attributed to the manufacturing of rocket fuel and explosives, Chilean nitrate fertilizer, and other naturally occurring sources.[5]

These contaminants target multiple organs, exhibiting carcinogenic, mutagenic, or endocrine disrupting properties. For example, nitrate can be converted to nitrite in the human body and can cause methemoglobinemia (i.e., blue baby syndrome), and nitrite can be transformed in vivo to potentially carcinogenic nitrosamines via nitrosation.[6, 7] Bromate was classified by the International Agency for Research on Cancer in Group 2B (possibly carcinogenic for humans).[8] The main risks are associated with the kidneys. Perchlorate is an endocrine disrupting compound (EDC) that interferes with iodine uptake by the thyroid gland and synthesis of thyroid hormones.[9] Current regulatory status of these oxyanions is listed in Table 1.1.

Table 1.1 Current regulatory status of selected oxyanions in drinking water.

Oxyanion	Regulation
Nitrate	MCL of 10 mg/L NO_3-N
Nitrite	MCL of 1 mg/L NO_2-N
Bromate	MCL of 10 µg/L as BrO_3^-
Perchlorate	NPDWR initiated in 2011
Chlorate	Listed on the CCL4

MCL: Maximum Contaminant Level
NPDWR: National Primary Drinking Water Regulations
CCL4: Contaminant Candidate List 4

In addition to conventional treatment technologies for oxyanions, including ion exchange and reverse osmosis which only serve to transfer the contaminant between phases, hydrogenation metal-based catalyst materials have emerged as a promising alternative. These materials enable reduction of oxyanion using $H_{2(g)}$, which can be generated from a variety of renewable sources. In the 1990s, Pd and Pd-Cu were identified in screening studies as the optimum catalysts for reduction of nitrite and nitrate, respectively.[10, 11] In a more recent screening study, a total of ten activated carbon-supported metal catalysts were prepared in house and tested for nitrate and nitrite reduction.[12] Pd, Ir, Pt, and Rh presented significant activities for nitrite reduction, and the activity was correlated with the hydrogen chemisorption energy per atom of metal. The study concluded that none of these metals is practically active for nitrate reduction by itself. Subsequently, 15 bimetallic catalysts were prepared and tested, with Rh-Cu showing the highest activity and producing a large amount of ammonium. Pd-Cu catalyst was considered most promising catalyst if selectivity to N_2 is desired.[12, 13] A large body of literature exists on nitrate reduction with Pd-based bimetallic catalysts.[14-21] Our current understanding of metal-catalyzed nitrate hydrogenation mechanisms has been limited mostly to reactions occurring with these materials. The prevailing reaction pathway follows a two-step process (Figure 1.1): (1) hydrogenation of nitrate to nitrite on bimetallic clusters followed by (2) further hydrogenation of

nitrite on Pd sites to a mixture of N_2 and NH_4^+ stable endproducts.[11, 18, 22-24] The proposed sequential reduction pathway is supported by the observation of nitrite as a transient reaction intermediate,[14, 25] increasing with pH as the rate of Pd-catalyzed nitrite reduction decreases,[22, 26] and isotope labeling experiments showing Pd-catalyzed reduction of NO to the same mixture of endproducts, but selective conversion of N_2O to N_2.[23] The distribution of endproducts, presumed to be controlled by the Pd-catalyzed reactions of nitrite or its daughter products (e.g., adsorbed NO), has been reported to vary with catalyst composition,[15] metal nanoparticle size,[27] support,[28] and solution pH.[29]
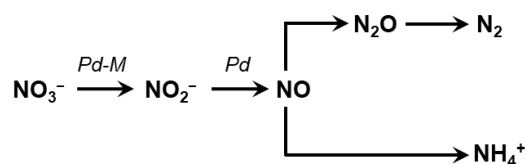
Figure 1.1 Nitrate hydrogenation pathway on Pd-based bimetallic catalysts.

Catalytic reduction of bromate was first studied with Ru oxide catalyst that couples bromate reduction with water oxidation, and adding an alcohol (e.g., methanol) as electron donor increases the reaction rate by promoting reduction of RuO_3 to catalytically active RuO_2.[30, 31] Chen and co-workers for the first time reported catalytic hydrogenation of bromate using H_2 as electron donor. Pd/Al_2O_3 exhibited higher activity than Pt/Al_2O_3, and the activity of Pd was found to be sensitive to Pd particle size.[32] The Pereira and Neves team assessed several monometallic catalysts supported on activated carbon for the catalytic reduction of bromate under hydrogen.[33] The Pd catalyst was found to be the most active when normalize by active metal mass, whereas other metals such as Pt surpass Pd if the activity is normalized to the available metal surface area. Among zeolite-supported catalysts comprising one or two of four metals, Pd, Cu, Th, and Rh, Pd-Cu bimetallic catalysts was concluded to be the most promising

catalyst.[34, 35] While Th also exhibits high activity, it is not suitable for use in water treatment processes due to its pyrophoricity and radioactivity. Pd catalyst with Cu as a secondary metal was also found to be the most active catalyst for bromate reduction among 10 combinations of a noble metal and a secondary non-noble metal screened, and the activity of Pd-Cu bimetallic catalyst was shown to depend on the atomic ratio between Pd and Cu.[36] Support also affects catalyst activity. Pd supported on Al_2O_3 showed higher activity than that on SiO_2 or activated carbon, which was attributed to its higher isoelectric point that enhances adsorption of the bromate anion under pH conditions tested.[32] The bromate reduction activity of different supported monometallic catalysts followed the trend TiO_2 > multiwall carbon nanotube (MWCNT) > activated carbon, with TiO_2 and MWCNT exhibiting catalytic activity by themselves.[37] In all studies of catalytic bromate reduction, stoichiometric reduction to bromide is observed with no detectable reaction intermediates.

In comparison to the other oxyanions, perchlorate is kinetically inert and few catalysts have been found to be active under ambient temperature and pressure conditions. In 2007, Pd-Re catalysts were first proposed to reduce perchlorate to chloride in water by H_2 under mild conditions.[38] The catalyst was prepared by adsorption of inorganic Re(VII) precursors onto Pd/C. Chloride is the only observed product with no detectable intermediates, and mechanistic investigations linked reduction to an oxygen atom transfer (OAT) mechanism catalyzed by the immobilized Re ions. Liu and co-workers promoted the development of this innovative technology by improving the design of catalyst to achieve significantly enhanced activity. The change of Re precursor from inorganic perrhenate (ReO_4^-) to organometallic oxorhenium complexes (e.g., *hoz*, or 2-(2'-hydroxyphenyl)-2-oxazoline) increased perchlorate reduction activity by approximately 100 fold.[39] By replacing Pd with Rh, the immobilized Re is also

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stabilized, presumably by reducing proposed intermediates (chlorate, chlorite, and hypochlorite) at a faster rate, thereby limiting reactions of these intermediates with Re that can lead to leaching of the Re complex from the support material.[40] The noble metal particles (i.e., Pd or Rh) serve to activate H_2 to reduce the oxidized Re(VII) complexes back to active Re(V) complex to complete the catalytic OAT cycle.[40] It has been reported that activity of carbon-supported monometallic catalysts follow the trend Rh/C > Pd/C > Ru/C.[40]

1.1.2 *N*-nitrosamines as emerging water contaminants and treatment options

In addition to inorganics, multiple organic compounds have also received attention due to their occurrence in water sources and health concern. Particularly, *N*-nitrosamines are a group of disinfection byproducts (DBPs)[41] that exhibit carcinogenicity and genotoxicity.[42] These compounds are widely detected in surface water, ground water, and treated water.[43-45] Although they are not currently regulated by NPDWR, U.S. EPA has included five *N*-nitrosamines on the CCL4,[46] and the World Health Organization (WHO) has established a guideline value of 0.1 µg L^{-1} for *N*-nitrosodimethylamine (NDMA) in drinking water.[47]

Physical treatment technologies are ineffective at removing *N*-nitrosamines. Adsorption of these compounds to activated carbon or soil is relatively insignificant, especially for lower molecular weight molecules like NDMA.[48, 49] They are also able to pass through membranes used for drinking water treatment including reverse osmosis membrane,[45, 50, 51] causing significant concern for potable reuse of municipal wastewater. Chemical destruction may be achieved by strongly oxidizing hydroxyl radicals generated in the advanced oxidation processes (AOPs).[52] However, *N*-nitrosamines are usually present at µg L^{-1} level, which is comparable to or much lower than the concentrations of non-target radical scavengers (e.g., natural organic

matter and bicarbonate) commonly found in water matrices, resulting in inefficient utilization of hydroxyl radical oxidants.

As *N*-nitrosamines are identified by a characteristic *N*-nitroso group, processes targeting to break the N-NO bond are promising for treating these recalcitrant contaminants. Several approaches have been reported effective for such purpose, including UV photolysis, metal reduction, and catalytic reduction (Figure 1.2). Among these approaches, UV photolysis is a common water treatment technology and has been applied at scale.[45, 53] Although it is relatively established, this technology has a major downside of high energy demand and cost associated with the required UV fluences, which are order-of-magnitude higher than those applied in disinfection processes.[45, 54] The *N*-nitrosamine removal efficiency by UV processes can be improved by hydrated electrons,[55] which requires adding elevated concentrations of photo-sensitizer such as KI. In contrast, both metal reduction and catalytic reduction reply on surface hydrogen atom as a reductant to break the N-NO bond. For example, zerovalent metals (e.g., Fe) form surface adsorbed atomic hydrogen upon water corrosion. This process is slow, and hazardous intermediates from *N*-nitrosamine reduction were observed to accumulate in the treated water.[56, 57] Earth-abundant metal Ni in the form of porous Raney Ni was found to be highly active at catalyzing *N*-nitrosamine reduction.[58] However, development of Ni materials for water treatment is limited by health concerns of Ni leached into treated water.[59] Pd-based catalysts have demonstrated fast kinetics and high stability for *N*-nitrosamine reduction.[60-62] As mentioned earlier, a major barrier for developing and adopting these catalysts for water treatment is the use of expensive Pd. Therefore, development of active, stable, and lower cost catalysts will be critical to advancing the treatment technology for *N*-nitrosamines.

Figure 1.2 Represenative approaches for transforming *N*-nitrosamines by breaking N-NO bond.

1.1.3 Supported Ruthenium catalysts and their applications

Pt group metals (Os, Ru, Ir, Rh, Pt, and Pd) are transition metals with high resistance to corrosion and widely used as catalysts.[63] Ru has historically had a lower price compared to other metals in Pt group[64] and found applications both as organometallic catalysts and supported metal catalysts.[65] Supported Ru catalysts have shown excellent performance in dehydrogenation,[66] oxidation,[67, 68] glycerol steam reforming,[69] and hydrogenolysis.[70] Particularly, recent studies applied supported Ru catalysts to a variety of hydrogenation reactions, including C_5 and C_6 sugars,[71, 72] organic acids (e.g., levulinic acid and lactic acid),[73, 74] benzene,[75] substituted arenes,[75, 76] and heteroaromatics (e.g., substituted furans).[77] The interest in Ru catalysts may be attributed to the growing research field of biomass conversion, where Ru catalysts have shown outstanding activity for the aqueous-phase hydrogenation of biosourced carbonyl compounds.[78]

Supported Ru catalysts have a distribution of surface sites that varies with particle size and shape. Understanding site-specific activity and developing controlled synthesis strategies are critical to the design of high-performance catalysts for reactions that are sensitive to catalyst structure. Ammonia synthesis and decomposition on Ru have been known to be structure-sensitive reactions, and B_5-type step sites have been identified to be the most active sites.[79] By controlling the pretreatment conditions of Ru/γ-Al₂O₃, Karim *et al*. obtained a suit of catalysts

differing in Ru particle size and shape.[80] Combining microscopy, chemisorption, and extended X-ray absorption fine structure (EXAFS) techniques, the Ru particle shape was reconstructed and shown to change from round for smaller particles to elongated or flat for larger particles. The number of B_5 sites highly depended on particle shape and increased with particle size up to 7 nm for flat nanoparticles, leading to the highest ammonia decomposition turnover frequency (TOF). The size-dependence of catalytic activity has also been observed for sugar hydrogenation using supported Ru catalysts.[71] Carbon-supported Ru particles of size ranging from 1 to 8 nm were prepared by incipient wetness impregnation and colloidal method, and the highest TOF was observed with a catalyst that has an average Ru particle size of ca. 3 nm. To differentiate the CO dissociation activity of step sites and terrace site of 2D-like Ru islands supported on rutile TiO_2, Liuzzi *et al*. blocked the step-edge sites of Ru by addition of boron.[81] Their results showed that initial reaction rate for B-doped Ru/TiO_2 was lower than that of non-doped Ru/TiO_2. Interestingly, the steady-state rates were identical for these two catalysts, indicating that the more active step-edge sites were modified under realistic Fischer–Tropsch synthesis conditions.

The major role of catalyst support is facilitating active metal phase dispersion to reduce metal loading and cost. Due to the close proximity with metal particles, catalyst support can also have an impact on metal activity and stability. Xiao *et al*. reported the synthesis of few-layer graphene (FLG)-supported Ru nanoparticle catalysts using a polyol approach and their high activity for levulinic acid hydrogenation.[73] The selectivity to γ-valerolactone was complete, and the catalysts demonstrated much higher stability compared with traditional activated carbon-supported Ru catalysts. The superior catalytic properties of FLG-supported Ru catalysts were attributed to greater metallic Ru content and large number of defects, where the sp^2 dangling bonds strongly interact with the dsp states of the Ru nanoparticles to mitigate nanoparticle

migration or aggregation. The ability of graphene to modulate electronic and geometric structures of Ru nanoparticles was also reported in other studies. For example, thermally exfoliated graphite oxide (TEGO)-supported Ru catalysts synthesized by incipient wetness impregnation imparted thermal stability to Ru nanoparticles heated at 700 °C in N_2 flow.[75] Ru nanoparticles on TEGO were observed to be more flat at high temperature reduction due to the strong interaction between Ru and TEGO. In addition, TEGO is a stronger electron-withdrawing support than carbon nanotubes, leading to relatively electron-deficient Ru nanoparticles and subsequently higher activities for benzene and *p*-chloronitrobenzene hydrogenation. Leng *et al*. observed chemoselective hydrogenation of nitrobenzene to aniline with C_{60}-supported Ru nanoparticles.[76] Density functional theory calculations suggested that the Ru nanoparticles supported on C_{60} are electron-deficient, consistent with experimental observations.

In addition to designing catalyst support, the controlled incorporation of other metals to Ru can also be utilized to tune catalytic properties. During levulinic acid hydrogenation in a 2-sec-butyl-phenol solvent, the catalytic properties of Ru/C were significantly modified by the addition of Sn.[82] Specifically, a catalyst containing equal amounts of Ru and Sn showed complete selectivity for levulinic acid hydrogenation versus the solvent and displayed stable time-on-stream activity. The ratio between Ru and Sn was found to be critical. While bimetallic Ru-Sn alloys had lower activity but improved stability, high loading of Sn led to β-Sn phase formation, which was not active for hydrogenation reactions and leached under reaction conditions. The bimetallic Ru-Fe catalysts were shown to achieve catalytic properties that differ from individual metals alone.[77] When hydrogenating multifunctional aromatic and heteroaromatic substrates, pure Ru nanoparticles exhibited selectivity following C=C > arene > C=O, while pure Fe nanoparticles were not active for hydrogenation reactions. At Fe contents in

the range of ca. 20−30%, the bimetallic nanoparticles exhibited selectivity following C=C > C=O >> arene. Bimetallic catalysts provide ample opportunities to new catalyst formulations and novel catalytic properties. Major challenges in the field include controlled synthesis of bimetallic nanoparticles and structure-activity relationship elucidation.[83]

Although Ru catalysts have received increasing attention in chemical synthesis and biomass conversion applications, the use of Ru catalysts for catalytic reduction water treatment remains very limited. The current focus of research is largely on Pd-based materials. The fact that Pd exhibits poor activity for reduction of selected contaminants, together with the scarcity and the high cost of this metal, necessitates an expansion of available catalyst formulations. Given the promising catalytic properties of supported Ru catalysts in hydrogenation reactions, their potential to be lower-cost alternative to Pd-based materials for water treatment applications should be explored.

1.1.4 Strategies for regenerating nitrate-contaminated ion exchange waste brine

Ion exchange is an established method for removing nitrate from drinking water. It has advantages including fast start-up, insensitivity to low temperature, stable operation, and ease of intermittent operation.[1, 84] However, this process requires large quantities of concentrated NaCl solution for resin regeneration, resulting in waste brine high in nitrate, chloride, and sulfate concentrations that requires further management. As a result, there is considerable interest in treating waste ion exchange brines to allow for brine re-use.

Efforts to biologically denitrify ion exchange waste brine have been pursued for over three decades. In the 1980s, Van der Hoek and co-workers proposed a combined ion exchange/biological denitrification process in which nitrate in ground water is removed by an ion exchange column and the resins are regenerated in a closed circuit through a biological

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denitrification reactor.[85-87] The process demonstrated a reduction of 95% in waste brine volume and a reduction of 80% in regeneration salt requirement.[87] Clifford and co-workers studied biological denitrification of spent regenerate brine in a sequencing batch reactor (SBR).[88-90] They examined higher sodium chloride concentration (0.5 N) and nitrate concentration (up to 835 mg NO_3^--N L^{-1}) than previous research effort and reported more than 95% denitrification within 8 h using an optimal methanol-to-nitrate-nitrogen ratio of 2.7. The salt consumption was lowered 50%, and the salt discharge can be reduced about 90%.[89] The authors further developed a mixed culture capable of rapidly reducing nitrate in 60 g L^{-1} NaCl, although the stability of the culture requires added sulfide, trace metals and phosphate.[91]

The main drawback of biological treatment of waste brine is public perception of the risk associated with microbes contaminating the drinking water supply. Additionally, biological treatment may also not be ideal for intermittent treatment applications, such as periodic treatment of ion exchange waste brines, due to slow start-up. Compared with biological treatment methods, chemical treatment options have the advantages of higher operational flexibility and minimal risk of microbial contamination in treated water. Among potential reducing agents, zero valent iron (ZVI) has relatively high efficiency and low cost. The majority of the studies with ZVI concluded nitrate is predominantly reduced to ammonia.[92-94] Studies of applying ZVI to nitrate reduction in brine matrix are limited. Although chloride is considered to induce corrosion of Fe^0 surface and thereby enhance reactivity or surface area,[95] elevated concentrations of NaCl (3-12 g L^{-1}) significantly slowed nitrate reduction with nanoscale ZVI.[96, 97] In a most recent study, however, high level of chloride (1.37 M) showed insignificant effect on nitrate reduction rate [92]. Despite fast kinetics and easy operation, the attractiveness of chemical reduction is compromised

by the requirement of highly excessive amount of ZVI (e.g., Fe to nitrate molar ratio >10)[98] and production of metal oxides waste sludge.

Compared with chemical reduction, catalytic reduction treatment leverages metal catalysts, which enhance reaction rate and enable the utilization of H_2 as a low cost and more sustainable electron donor than the carbon-based donors typically employed in biological denitrification schemes.[99] Fast kinetics also decreases the volume and footprint of the reactor. Pintar and co-workers first proposed a closed loop ion exchange-catalyst system for brine reuse, in which a 0.25-1 wt% NaCl solution was continuously circulated through the catalyst column and resin column until all nitrate was removed.[100] Alternatively, our group proposed a two-stage hybrid treatment system in which ion exchange process is used for treating nitrate contaminated water source and the exhausted resins are regenerated by using fresh brine or waste brine that is catalytically treated with Pd-In/C in a separate reactor (Figure 1.3).[99, 101] The catalytic reduction treatment was investigated in batch reactor, fixed bed reactor (FBR) or trickle bed reactor (TBR).[99, 101, 102] A separate catalytic reactor is more readily incorporated into current ion exchange process without the need to resizing of the ion exchange column. Elevated levels of non-target ions such as chloride and sulfate were found to inhibit catalyst activity.[99, 100] A major limitation of catalytic treatment process is the high capital cost of Pd-based catalysts. Efforts have also typically focused on converting nitrate to N_2 over the NH_4^+ endproduct. However, conversion to NH_4^+ may, in fact, be advantageous if a suitable process for recovering the endproduct as a fertilizer product (e.g., $(NH_4)_2SO_4$) is available.
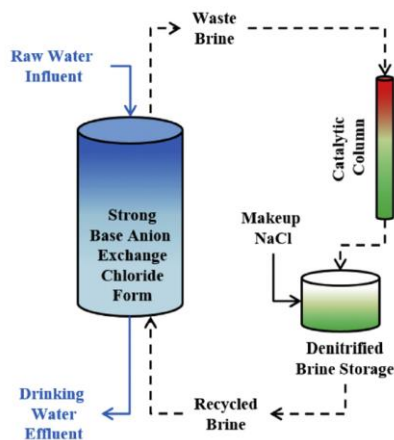
Figure 1.3 Flow diagram of the hybrid ion exchange-catalyst treatment system. Reproduced from Bergquist *et al.*[101]

1.2   Main Objectives

This dissertation was designed to address challenges raised in the development of catalytic reduction technologies, namely identifying alternatives to Pd-based catalysts and integration of catalytic treatment into existing treatment processes like ion exchange. The main goals of the dissertation were to develop catalysts and processes to advance the application of catalytic reduction water treatment technologies. The specific objectives and hypotheses of this research are as follows:

1. *Assess selected Pt group metals for their activity, solution pH dependence, scope of substrate reactivity, and economic benefit with a suite of oxyanions (chapter 2).* Pd-based catalysts have been studied for their activity in catalyzing the hydrogenation of oxyanions. I hypothesize that other Pt group metals, such as Ru, Rh, Ir, and Pt, will show activity in reducing one or multiple oxyanion contaminants of concern, including nitrate, bromate and chlorate. I also anticipate that some of these metals can be combined with Re (an oxygen atom transfer catalyst) to achieve reduction of perchlorate, a kinetically inert oxyanion. I also hypothesize that catalyst activity and

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its dependence on solution pH will be determined by the identity of metal and less affected by the support.

2. *Evaluate the kinetics and investigate the mechanism of nitrate and nitrite reactions with supported Ru catalysts (chapter 3).* Catalyst screening experiments revealed that Ru/C has unexpectedly higher activity of nitrate reduction than other Pt group metals. The reactivity and mechanistic features of reactions on Ru catalyst surfaces is unknown. I hypothesize that the high activity observed here results from high dispersion of Ru nanoparticles in commercial catalysts and catalyst pretreatment protocols that restore Ru surfaces to their active form. I also hypothesize that nitrate reacts by a similar mechanism observed for Pd-based bimetallic catalysts.

3. *Extend the evaluation of Ru catalyst activity to N-nitrosamines and other trace organic water contaminants (chapter 4).* Previously, bimetallic Pd catalysts that react with nitrate have been shown to also reduce NDMA to less toxic products. Thus, I hypothesize that Ru catalysts that are reactive with nitrate and nitrite will also exhibit high reactivity with NDMA and related *N*-nitrosamines. Likewise, I expect reactivity will extend, to varying degrees, other classes of organic pollutants where Pd catalyst activity has been previously documented (e.g., halo- and nitro-organics).

4. *Develop integrated process coupling ion exchange, catalytic nitrate reduction, and membrane distillation to treat nitrate-contaminated water sources while reducing brine consumption and producing a value-added fertilizer product (chapter 5).* Reuse of waste brine from regenerating ion exchange resin has been studied with bimetallic Pd catalysts, which reduces concentrated nitrate in the brine to a mixture of nitrogen gas and ammonia. The production of ammonia has typically been deemed as

undesirable but appears to be unavoidable due to the nature of catalyst and limitation of hydrogen transfer. I hypothesize that substitution of Pd-based catalysts with Ru catalysts will be technically feasible to remove nitrate from waste brine and be economic competitive due to the much lower cost of Ru. I further hypothesize that integrating a third process, membrane distillation, will enable recovery of the ammonia byproduct as ammonium sulfate, $(NH_4)_2SO_4$, a commercial fertilizer product.

In addition to the dissertation's major topic, I extended my research scope to include renewable energy and leveraged catalysis and process integration to produce a performance-advantaged renewable hydrocarbon diesel blendstock from low-cost, biologically-derived butyric acid. Renewable diesel fuel is critical to reducing the carbon footprint of the transportation sector, and lignocellulosic biomass is a particularly promising non-food feedstock for such applications. Short-chain carboxylic acids are among the most abundant bio-intermediates from anaerobic fermentation of lignocellulosic sugars. In chapter 6, a C_{14} hydrocarbon molecule is predicted to exhibit desired fuel characteristics, and its synthesis is demonstrated from upgrading butyric acid through sequential catalytic reaction pathways.

1.3   Intellectual Merits and Broader Impacts

This research work will contribute to a better understanding of catalytic reduction treatment technology from both fundamental science and process design perspectives. It will improve fundamental understanding of multiple Pt group hydrogenation metals for reducing aqueous oxyanion contaminants with different reactivity. Particularly, for the first time, it will reveal the activities of Ru catalysts for a range of inorganic and organic molecules in aqueous phase under ambient temperature and hydrogen at atmospheric pressure and the relationship

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between catalyst physical and chemical properties with catalyst activity. This research will also demonstrate an engineering strategy for simultaneous water purification and resource recovery by combining catalysts with physical separations technologies.

This research work will have several broader impacts. It will facilitate the future rational selection of metal catalyst for oxyanion contaminants, providing a suite of options that can be modified based on prevailing market prices. The results will also provide useful guidance for the development of lower cost Ru-based catalysts for various water treatment applications, as both stand-alone or hybrid systems. Outcomes from this work will provide a path forward for the further development and deployment of practical catalytic water processing technologies.

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CHAPTER 2

EXPLORING BEYOND PALLADIUM: CATALYTIC REDUCTION OF AQUEOUS
OXYANION POLLUTANTS WITH ALTERNATIVE PLATINUM GROUP METALS AND
NEW MECHANISTIC IMPLICATIONS

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2.1   Abstract

For over two decades, Pd has been the primary hydrogenation metal studied for reductive
catalytic water treatment applications. Herein, we report that alternative platinum group metals
(Rh, Ru, Pt and Ir) can exhibit substantially higher activity, wider substrate selectivity and
variable pH dependence in comparison to Pd. Cross comparison of multiple metals and oxyanion
substrates provides new mechanistic insights into the heterogeneous reactions. Activity
differences and pH effects mainly originate from the chemical nature of individual metals.
Considering the advantages in performance and cost, results support renewed investigation of
alternative hydrogenation metals to advance catalytic technologies for water purification and
other environmental applications.

2.2 Introduction

Toxic oxyanions, such as BrO_3^-, ClO_3^-, NO_3^- and ClO_4^-, are ubiquitous drinking water contaminants originating from both anthropogenic and natural sources,[1-4] or are generated during water treatment processes (e.g., chlorination, ozonation, desalination, and electrochemical treatment).[5-9] These ions target multiple organs, and can have carcinogenic, mutagenic, and/or endocrine disrupting properties.[10-12] Ion exchange is the primary technology used to treat oxyanion-contaminated water; reverse osmosis is also used when salt removal is required. These technologies effectively serve to either trap the contaminants in a resin matrix, or to concentrate the contaminants in a waste brine. Thus, it would be preferable to apply destructive treatment technologies to convert oxyanions into less toxic or innocuous end products (e.g., Br^-, Cl^- and N_2), contributing to more sustainable drinking water treatment processes.[13-16]

Pd-based heterogeneous catalysis has garnered significant attention as a potential strategy for reduction of oxyanions and other highly oxidized contaminants (e.g., halogenated and nitro organics).[17] Ever since 1993 when Pd was identified as the "optimum" hydrogenation metal for water treatment applications (based on the screening of hydrogenation metals for nitrite reduction[18]), research efforts have reported on many aspects of Pd-based catalysis, including the effects of Pd nanoparticle size and morphology,[19] catalyst supports,[20-23] bimetallic formulations for treating recalcitrant substrates,[14, 24, 25] water matrix effects,[26, 27] and pilot-scale field testing .[28-30] We argue here that the narrow focus on Pd has limited advancement of reductive water treatment catalyst technologies. Little effort has been devoted to investigating water treatment applications with periodically related hydrogenation metals, e.g., Rh, Ru, Pt and Ir, which have seen many advances in other areas of catalytic science, including organic synthesis,[31] biomass valorization,[32] and vehicle exhaust gas conversion.[33]

In recent screening studies by the Pereira and Neves team,[34-38] several hydrogenation metals were evaluated for BrO_3^- and NO_3^- reduction, and Pd-based catalysts were still reported as having the highest activity. However, our group recently found that a Rh/C catalyst exhibited substantially higher activity than Pd/C for ClO_3^- reduction in acidic solution.[39] In literature, Rh/Al_2O_3[40-42] and Pt/C[43] also exhibit unique activities, such as hydrodefluorination, that the corresponding Pd-based catalysts do not. These findings suggest that other hydrogenation metals besides Pd may have unique catalyst attributes that could benefit individual water treatment applications and therefore deserve renewed attention.

Herein we report results of a series of catalytic water treatment experiments comparing the activities of alternative platinum group metals (supported on activated carbon or alumina) for reduction of four oxyanion contaminants with a broad range of chemical reactivity (BrO_3^- >> ClO_3^- > NO_3^- >> ClO_4^-). Rh exhibits substantially higher activity than Pd during reduction of BrO_3^-, ClO_3^- and NO_3^-. Ru, with a substantially lower cost compared to the other four metals (Pd, Rh, Pt and Ir), shows unique pH insensitivity and the highest activity for ClO_3^- and NO_3^- reduction at circumneutral pH conditions. All five metals are also able to reduce ClO_4^- when combined with Re species as bimetallic Re−M/C catalysts. Cross comparison of multiple oxyanion substrates and metals reveals new mechanistic insights and suggest new directions to develop novel catalysts for challenging water contaminants.

2.3   Experimental

2.3.1   Chemicals and materials

Unless otherwise specified, all chemicals and metal catalysts (nominal 5 wt% or 1 wt% hydrogenation metal nanoparticles dispersed on activated carbon and alumina supports) were purchased from Sigma−Aldrich or Alfa−Aesar. Detailed catalyst information and

characterization data are shown in Table 2.1. The Ru/Al$_2$O$_3$ catalyst required a pretreatment (1 atm H$_2$ flow in a tube furnace under 350 °C for 2 h) for metal reduction and activation of oxyanion reduction activity.[44] Aqueous solutions were prepared using deionized (DI) water (resistivity 18.2 MΩ cm). H$_2$ gas (99.9999% UHP, Matheson) was used for catalytic reactions.

2.3.2 Catalytic reduction of oxyanion contaminants

2.3.2.1 Bromate (BrO$_3^-$)

In a 50-mL pear-shaped flask (round bottom, 24/40 joint), a magnetic stir bar, 5 mg of catalyst (dry weight basis), and 50 mL of DI water were added and sonicated for 1 min to make a 0.1 g L^{-1} catalyst suspension. A rubber stopper loaded with two 16 gauge stainless needles capped the flask. H$_2$ was sparged through one needle below the liquid surface, and the head space was open to the atmosphere through another needle above the liquid surface. All batch reactions were conducted under 1 atm H$_2$ at room temperature (20-22 °C). The solution pH was adjusted by 1 mM HCl (pH 3.0), 0.5 mM Na$_2$HPO$_4$ plus 0.5 mM NaH$_2$PO$_4$ (pH 7.2), or 0.5 mM NaHCO$_3$ plus 0.5 mM Na$_2$CO$_3$ (pH 10.3). The possible competive adsorption of buffer anions with oxyanions on catalyst surface was not considered and may require further evaluation. Tests showed that these buffers were sufficient to maintain the pH for BrO$_3^-$ and ClO$_3^-$ reductions. After the suspension was pre-sparged for 1 h to pre-reduce any surface oxides present on the immobilized metal nanoparticles, the reaction was initiated by adding 1 mL of the 50 mM NaBrO$_3$ stock solution (C$_0$ = 1 mM). For the rapid BrO$_3^-$ reduction reactions, a high H$_2$ flow rate (~100 mL min^{-1}) was necessary to observe pseudo-first-order kinetics in the batch experiments. Samples were collected at periodic time intervals using a 3-mL syringe introduced through the H$_2$ outlet needle, and the collected aliquot was immediately filtered (0.45-µm nylon membrane) to quench the reaction before subsequent analysis of the filtrate sample.

2.3.2.2 Chlorate (ClO3⁻)

The reaction setup was the same as for BrO_3^- reduction, except that the catalyst loading in the suspension was increased to 0.5 g L^{-1} because initial tests showed this oxyanion to generally exhibit lower reactivity with the catalysts. H_2 gas flow rates higher than ~20 mL min⁻¹ did not increase reaction rates. An aliquot of $KClO_3$ stock solution (50 mM, 1 mL) was added to the reactor to initiate individual batch reactions with $C_0 = 1$ mM.

2.3.2.3 Nitrate (NO3⁻)

The reaction setup was the same as for ClO_3^- reduction, and a $NaNO_3$ stock solution (50 mM) was added to initiate batch reactions with $C_0 = 1$ mM. The pH was stabilized using higher buffer concentrations [1 mM HCl plus 10 mM H_3PO_4 (pH pre-adjusted with NaOH to 3.0), 5 mM Na_2HPO_4 plus 5 mM NaH_2PO_4 (pH 7.2), or 5 mM $NaHCO_3$ plus 5 mM Na_2CO_3 (pH 10.3)] because NO_3^- reduction consumes one (N_2 product, Eq. 2.1) or up to two equivalents of H^+ (NH_4^+ product, Eq. 2.2).[14]

$$NO_3^- + 2.5\ H_2 + H^+ \rightarrow 0.5\ N_2 + 3\ H_2O \tag{2.1}$$

$$NO_3^- + 4\ H_2 + 2\ H^+ \rightarrow NH_4^+ + 3\ H_2O \tag{2.2}$$
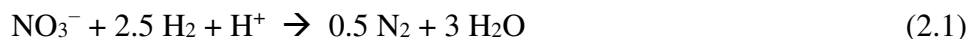
2.3.2.4 Preparation of Re−M/C and reduction of perchlorate (ClO4⁻)

In a 50-mL pear shape flask, a magnetic stir bar, 50 mg of M/C catalyst and 25 mL of DI water (pH pre-adjusted to 3.0 using 1 mM HCl) were added and sonicated for 1 min to yield a 2.0 g L^{-1} catalyst suspension. A NH_4ReO_4 stock solution (5000 ppm as Re, 0.5 mL) was added to the M/C catalyst suspension to reductively immobilize Re ($C_T = 100$ ppm) into the porous carbon support matrix under H_2 sparging (flow rate ~10 mL min⁻¹). The immobilization process was monitored by measuring dissolved ReO_4^- in filtered water samples with ion chromatography until concentrations were below detection.[14] Overnight sparging with H_2 led to complete

immobilization of Re and yielded bimetallic catalysts containing 5 wt% Re. Reactions with ClO_4^- were then initiated by adding an aliquot of $NaClO_4$ stock solution (200 mM, 0.625 mL) to the suspension (C_0 = 5 mM). Samples were collected and filtered using the same procedures described above.

2.3.3 Water sample analysis

The concentrations of BrO_3^-, Br^-, ClO_3^-, Cl^-, and NO_3^- were determined by a Dionex ICS-3000 ion chromatography system (25-μL injection loop and a suppressed conductivity detector). An IonPac AS19 column maintained at 30 °C was used as the stationary phase and 10 mM KOH at 1.0 mL min^{-1} was the eluent. The concentrations of ClO_4^- and ReO_4^- were analyzed by a Dionex ICS-2000 ion chromatography system (25-μL injection loop and a suppressed conductivity detector). An IonPac AS16 column maintained at 30 °C was used as the stationary phase and 65 mM KOH at 1.2 mL min^{-1} was the eluent.

2.3.4 Catalyst characterization

Specific surface area (BET method) and average pore size (BJH method) of the catalyst support materials were measured by N_2 physisorption with a Micromeritics ASAP 2020 analyzer. Dispersion of the hydrogenation metals was determined by chemisorption based on literature methods[45-47] with a Micromeritics AutoChem II analyzer equipped with a thermal conductivity detector. Results of physisorption and chemisorption measurements are summarized in **Table 2.1**. To determine surface zeta potentials of selected catalysts under varied pH and the H_2 atmosphere, catalyst suspensions (0.5 g L^{-1}) containing different pH buffers (as described in 2.2.1) were sparged with 1 atm H_2 for 30 min, and immediately transferred into an anaerobic glovebox (97% N_2, 3% H_2; Coy Laboratories). An aliquot of suspension was then transferred into a cuvette and sealed with the plastic cap before analyzing for zeta potential (Malvern Zetasizer Nano ZS).

2.3.5 Kinetic data analysis

Under the reaction conditions described above, reduction of all oxyanion contaminants generally followed a pseudo-first-order rate law for at least two half-lives (i.e., 75% decay). The initial turnover frequency (TOF$_0$, min^{-1}), which represents the number of oxyanion molecules reduced per surface metal site per minute, was calculated by Eq. 2.3:[19]

$$TOF_0 = \frac{kC_0}{C_{surface\ metal}} = \frac{kC_0 M_{metal}}{C_{total\ metal} D_{metal}} \tag{2.3}$$

where k is the measured pseudo-first-order rate constant (min^{-1}) for oxyanion reduction in the batch reaction, C_0 is the initial oxyanion concentration (mol L^{-1}), $C_{surface\ metal}$ is the concentration of surface metal in the catalyst suspension (mol L^{-1}), M_{metal} is the molar mass of metal element (g mol^{-1}), $C_{total\ metal}$ is the total concentration of metal loaded in the catalyst suspension (g L^{-1}), and D_{metal} is the metal dispersion on the catalyst support material (Table 2.1), representing the fraction of metal atoms exposed on the surface of the dispersed metal nanoparticles.

2.4 Results and Discussion

2.4.1 Catalytic reduction of bromate

Figure 2.1a shows catalytic reduction of bromate (BrO$_3^-$) at pH 7.2 by the five activated carbon supported metal catalysts [M/C, 0.1 g L^{-1} catalyst loading with nominal 5 wt% (Pd, Pt, Rh, Ru) or 1 wt% (Ir) of each metal]. A good mass balance between BrO$_3^-$ and Br$^-$ is obtained for each catalyst (Figure A.1 in Appendix A), demonstrating complete BrO$_3^-$ reduction with negligible accumulation of BrO$_x^-$ (x<3) intermediates Eq. 2.4.

$$BrO_3^- + 3\ H_2 \rightarrow Br^- + 3\ H_2O \tag{2.4}$$
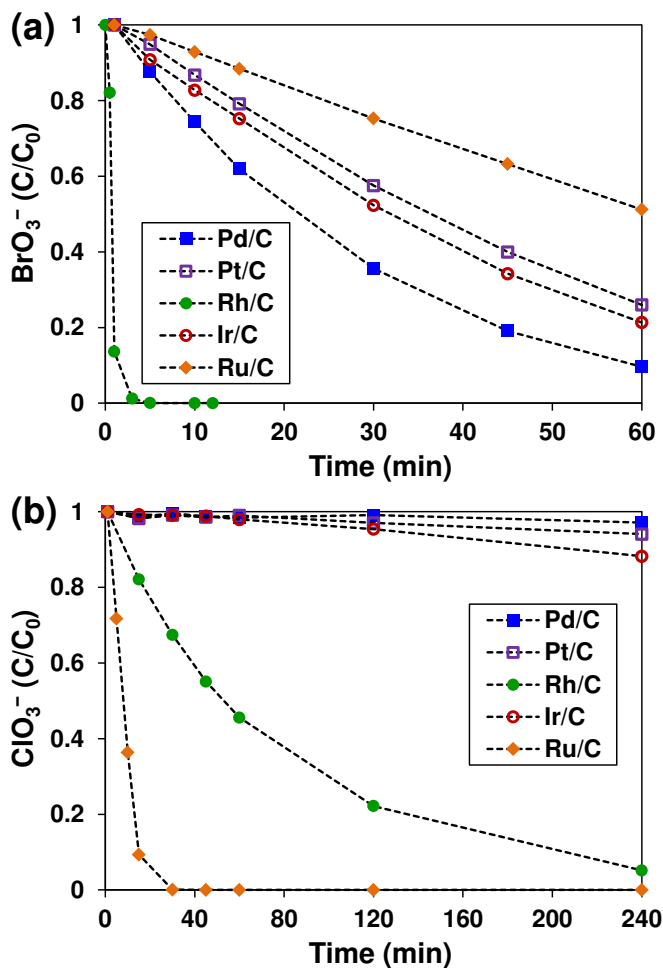
Figure 2.1 Timecourse profiles with for reduction of (a) 1 mM BrO_3^- by 0.1 g L^{-1} M/C catalysts and (b) 1 mM ClO_3^- by 0.5 g L^{-1} M/C catalysts with 1 atm H_2 at pH 7.2 and 22 °C (nominal 5 wt% metal for Pd, Rh, Ru, and Pt; 1 wt% metal for Ir).

Comparing the observed BrO_3^- reduction profiles shows that Rh/C is substantially more active than the other four M/C catalysts. At the catalyst loading of 0.1 g L^{-1}, the reduction of 1 mM BrO_3^- is complete within 5 min. The activity of Rh/C is much higher than most supported hydrogenation metal catalysts reported to date when compared on a metal mass-normalized basis.[34, 36-38, 48, 49] Since the metal dispersion of individual catalysts differ (Table 2.1), the activities of hydrogenation metals are further compared using initial turnover frequency values (TOF_0, Eq. 2.3). As shown in Table 2.2, Rh/C exhibited significantly higher TOF_0 than other

catalysts at pH 7.2. Although the apparent reactivity of Ir/C with BrO_3^- is slightly lower than that of Pd/C (Figure 2.1a), Ir/C exhibited the second highest TOF_0. Thus, the catalysts incorporating the two Group 9 metals, Rh and Ir, show the highest activity for BrO_3^- reduction at neutral pH conditions that are highly relevant for water treatment systems.

Acidic pH conditions have been previously reported to accelerate BrO_3^- reduction by Pd catalysts.[20, 48] To examine if this trend extends to other hydrogenation metals, BrO_3^- reduction by all five M/C catalysts was also measured at pH 3.0. Results from these experiments (Table 2.2 and Figure A.2a in Appendix A) show that catalysts incorporating the two Group 10 metals, Pd and Pt, exhibit significant pH dependence, with TOF_0 increasing by more than an order of magnitude when pH is lowered from 7.2 to 3.0. In comparison, the catalysts incorporating Group 9 (Rh and Ir) and Group 8 (Ru) metals show less activity change when pH is lowered. TOF_0 for Rh/C and Ru/C decrease by 35-40%, and Ir/C increases 3-fold when the pH is lowered from 7.2 to 3.0.

2.4.2 Catalytic reduction of chlorate

Results for catalytic reduction of chlorate (ClO_3^-) by M/C at pH 7.2 are shown in Figure 2.1b. In comparison to BrO_3^-, ClO_3^- is much more inert to reduction (note that the suspension catalyst loading used in the experiments was increased to 0.5 g L^{-1}). Like BrO_3^-, a good mass balance with ClO_3^- and Cl^- (Figure A.3 in Appendix A) is observed during reactions, consistent with the following reaction Eq. 2.5 and confirming negligible accumulation of ClO_x^- (x<3) intermediates.

$$ClO_3^- + 3\ H_2 \rightarrow\ Cl^- + 3\ H_2O \qquad\qquad (2.5)$$

The highest apparent reactivity with ClO_3^- is observed with Ru/C, a Group 8 metal, and the resulting TOF_0 (6.0 min^{-1}) is substantially higher than catalysts incorporating the other four

Table 2.1 Catalyst information and characterization data

Entry	Metal	Supplier and catalog number	Surface area ($m^2\,g^{-1}$)	Average pore size (nm)	Metal dispersion	Metal particle diameter (nm)
		Activated Carbon Support				
1	5 wt% Pd	Sigma−Aldrich #205680	958	3.1	30.3%	3.7
2	5 wt% Rh	Sigma−Aldrich #206164	870	3.6	31.3%	3.5
3	5 wt% Ru	Alfa−Aesar #44338	704	3.4	11.2%	11.8
4	5 wt% Pt	Sigma−Aldrich #205931	1370	3.4	23.9%	4.7
5	1 wt% Ir	Alfa−Aesar #38330	839	3.3	31.8%	3.7
		Alumina Support				
6	5 wt% Pd	Sigma−Aldrich #205710	106	8.9	66.3%	1.7
7	5 wt% Rh	Sigma−Aldrich #212857	168	10.0	64.1%	1.7
8	5 wt% Ru	Sigma−Aldrich #381152	93	15.3	9.8%	13.5
9	5 wt% Pt	Sigma−Aldrich #205974	94	9.2	23.4%	4.8

Table 2.2 Initial turnover frequencies for the reaction of 1 mM oxyanions with M/C, M/Al$_2$O$_3$

Entry	Catalyst	Catalytic oxyanion reduction turnover frequency (TOF$_0$, min^{-1})[a]					
		BrO$_3^-$		ClO$_3^-$		NO$_3^-$	
		pH 7.2	pH 3.0	pH7.2	pH 3.0	pH 7.2	pH 3.0
1	Pd/C (*10*)[b]	2.7 ± 0.1[c]	33.4 ± 2.7	0.0012 ± 0.0005	0.070 ± 0.002	ND[d]	ND
2	Rh/C (*9*)	54.4 ± 5.5	32.3 ± 0.6	0.17 ± 0.01	6.7 ± 0.5	0.0019 ± 0.0001	0.046 ± 0.004
3	Ru/C (*8*)	2.0 ± 0.1	1.3 ± 0.5	6.0 ± 1.1	0.11 ± 0.01	0.33 ± 0.01	0.71 ± 0.01
4	Pt/C (*10*)	3.7 ± 0.1	42.9 ± 0.4	0.0076 ± 0.0010	0.090 ± 0.006	ND	ND
5	Ir/C (*9*)	15.5 ± 0.5	47.0 ± 1.9	0.061 ± 0.003	1.2 ± 0.1	ND	ND
6	Pd/Al$_2$O$_3$	0.83 ± 0.01		ND		ND	
7	Rh/Al$_2$O$_3$	5.9 ± 0.6		0.014 ± 0.001		0.0025 ± 0.0001	
8	Ru/Al$_2$O$_3$	7.0 ± 0.4		1.1 ± 0.1		0.30 ± 0.02	
9	Pt/Al$_2$O$_3$	6.5 ± 0.3		0.0058 ± 0.0001		ND	

[a]Determined for catalyst reactions with 1 mM oxyanions, 22°C, continuous mixing and sparging with 1 atm H$_2$. 0.1 g L^{-1} catalyst suspensions used for reactions with BrO$_3^-$, 0.5 g L^{-1} used for ClO$_3^-$ and NO$_3^-$.

[b]Number in parenthesis indicate the Periodic Table group number of the hydrogenation metal.

[c]Errors represent 95% confidence intervals.

[d]Meaningful catalytic activity not detected within the 4 h of reaction at the 0.5 g L^{-1} catalyst loading.

Group 9 and 10 metals (Table 2.2), due, in part, to the low dispersion of Ru nanoparticles on the carbon support. TOF_0 values measured for the two Group 9 metals (0.17 min^{-1} for Rh and 0.061 min^{-1} for Ir) are higher than those observed for the two Group 10 metals (< 0.01 min^{-1} for Pd and Pt). Thus, for neutral pH conditions, periodic trends suggest that ClO_3^- reactivity follows Group 8 >> Group 9 >> Group 10 metals.

Comparing pH dependences for ClO_3^- reactions with the different M/C reveals some other interesting trends. Catalysts incorporating the Group 9 and 10 metals show significantly enhanced reactivity with ClO_3^- under acidic pH conditions compared to pH 7.2 (Figure A.2b in Appendix A and Table 2), whereas reactions are inhibited under these conditions for Ru, the Group 8 metal. At pH 3.0, Rh/C is the most active catalyst for ClO_3^- reduction (TOF_0 increases from 0.17 min^{-1} at pH 7.2 to 6.7 min^{-1}). A mirror trend is observed for Ru/C, where TOF_0 decreases from 6.0 min^{-1} at pH 7.2 to 0.11 min^{-1} at pH 3.0. The unique pH dependence observed for Ru/C suggests different rate-controlling surface reaction mechanisms for this catalyst compared to those incorporating Group 9 and 10 metals.

2.4.3 Catalytic reduction of nitrate

Of the catalysts examined, only Rh/C and Ru/C show meaningful reactivity with the more recalcitrant nitrate ion (NO_3^-) in 0.5 g L^{-1} catalyst suspensions monitored for 4 h. As shown in Table 2.2 and Figure A.4 in Appendix A, Ru shows much higher activity than Rh, and both metals exhibit enhanced activities when pH is reduced from 7.2 to 3.0. The observed product of NO_3^- reduction by these two metals under the test conditions is mostly NH_3/NH_4^+ (Eq. 2.2) rather than the desired N_2 (Eq. 2.1). Nevertheless, results show that monometallic Rh and Ru catalysts are capable of reducing NO_3^- without the need for secondary promoter metals (e.g., In, Cu, Sn, and Re) used to activate Pd catalysts towards NO_3^- reduction [14, 18, 25]. Motivated by the

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low market price of Ru ($1.4 g^{-1}) in comparison to the other metals ($17 to $38 g^{-1}) (Table A.1), an in-depth study of Ru-catalyzed NO$_3^-$ and NO$_2^-$ reduction by our team was undertaken and reported separately.[44]

2.4.4 Effect of metal catalyst support materials

We also examined reactions of the three tri-oxy anions with Pd, Pt, Rh, and Ru supported on porous alumina (M/Al$_2$O$_3$), another common catalyst support material, and found generally the same reactivity trends observed for the M/C catalysts. Alumina is unstable under acidic pH conditions, so reactivity was only compared with M/C at pH 7.2. Compared to activated carbon support materials, the alumina supports generally have an order of magnitude lower specific surface areas and two times larger pore average size (Table 2.1). As shown in Figure 2.2 and Table 2.2, M/Al$_2$O$_3$ catalysts generally exhibit similar activity compared to the corresponding M/C.

Still, the highest activity for BrO$_3^-$ reduction at pH 7.2 is observed with both Rh/C and Rh/Al$_2$O$_3$, and the highest activity for ClO$_3^-$ and NO$_3^-$ reduction is observed with both Ru/C and Ru/Al$_2$O$_3$. These similar trends suggest that activity differences among the catalysts primarily originate from the chemical nature of the immobilized metal nanoparticles, and the effects of the support materials may be minor.

2.4.5 Catalytic reduction of perchlorate

For the tetra-oxyanion perchlorate (ClO$_4^-$), the most inert of the target oxyanions examined, no reaction is observed using any of the monometallic catalysts (Table A.2 in Appendix A). We previously reported on preparation of bimetallic Re−Pd/C catalysts that are able to reduce aqueous ClO$_4^-$ because the immobilized surface oxorhenium(V) species [from the catalytic reduction of oxorhenium(VII) with Pd/C, Eq. 2.6] are able to abstract the most

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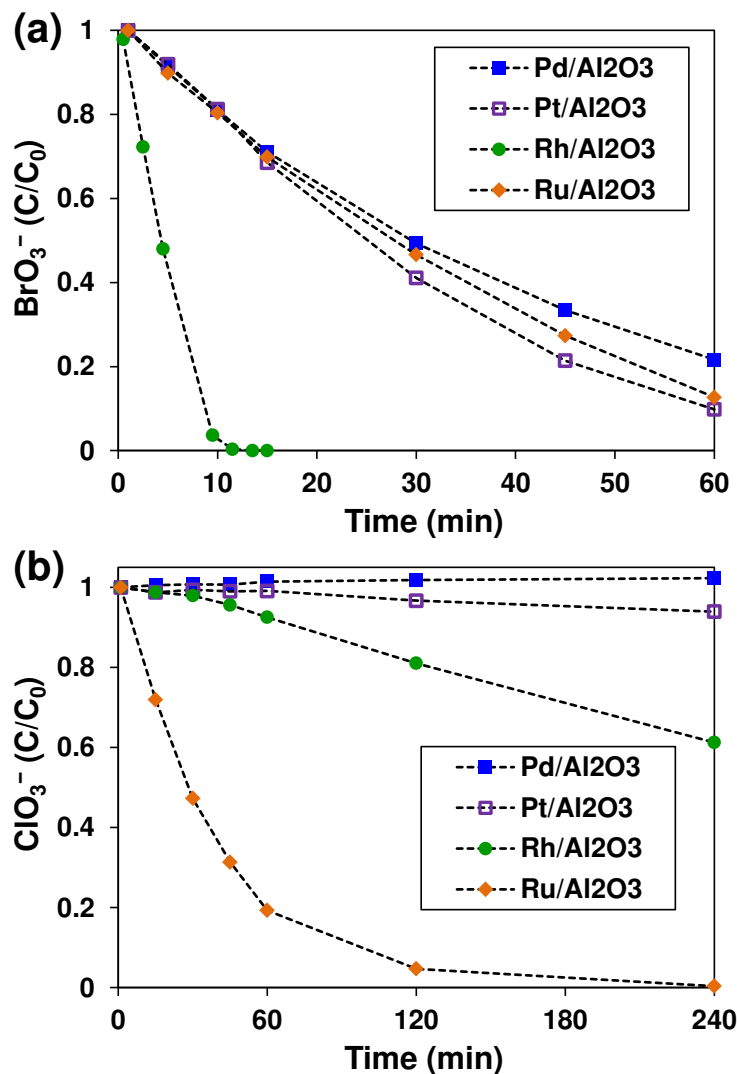
Figure 2.2 Timecourse profiles with for reduction of (a) 1 mM BrO_3^- by 0.1 g L^{-1} M/Al_2O_3 catalysts and (b) 1 mM ClO_3^- by 0.5 g L^{-1} M/Al_2O_3 catalysts with 1 atm H_2 at pH 7.2 and 22 °C (nominal 5 wt% metal for all catalysts).

challenging oxygen atom, via oxygen atom transfer (OAT) reaction, converting ClO_4^- to ClO_3^- (Eq. 2.7), which is further reduced to Cl^- (Eq. 2.8) by OAT with Re^V or directly by reaction with hydrogenation nanoparticles (Figure 2.3a).[39, 50, 51]

$$Re^{VII}(O)_n + H_2 \rightarrow Re^V(O)_{n-1} + H_2O \qquad (2.6)$$

$$ClO_4^- + Re^V(O)_{n-1} \rightarrow ClO_3^- + Re^{VII}(O)_n \qquad (2.7)$$

$$ClO_3^- + 3\ H_2 \rightarrow\rightarrow\rightarrow\ Cl^- + 3\ H_2O \qquad (2.8)$$
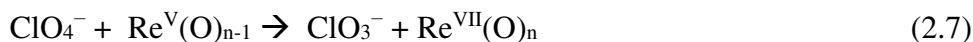
And thus the overall reaction is

$$ClO_4^- + 4\ H_2 \rightarrow Cl^- + 4\ H_2O \qquad (2.9)$$

In order to assess the dependence of ClO_4^- reduction on the other four hydrogenation metals, we followed the same approach for bimetallic catalyst synthesis[14, 52] to prepare Re−M/C catalysts using each of the M/C catalysts discussed already. Figure 2.3b shows the reactivity of 5 mM ClO_4^- with 2 g L^{-1} of each Re−M/C catalyst. The apparent reactivity of the bimetallic catalysts follows Re−Pd/C > Re−Ru/C > Re−Rh/C > Re−Ir/C > Re−Pt/C. Mechanistic
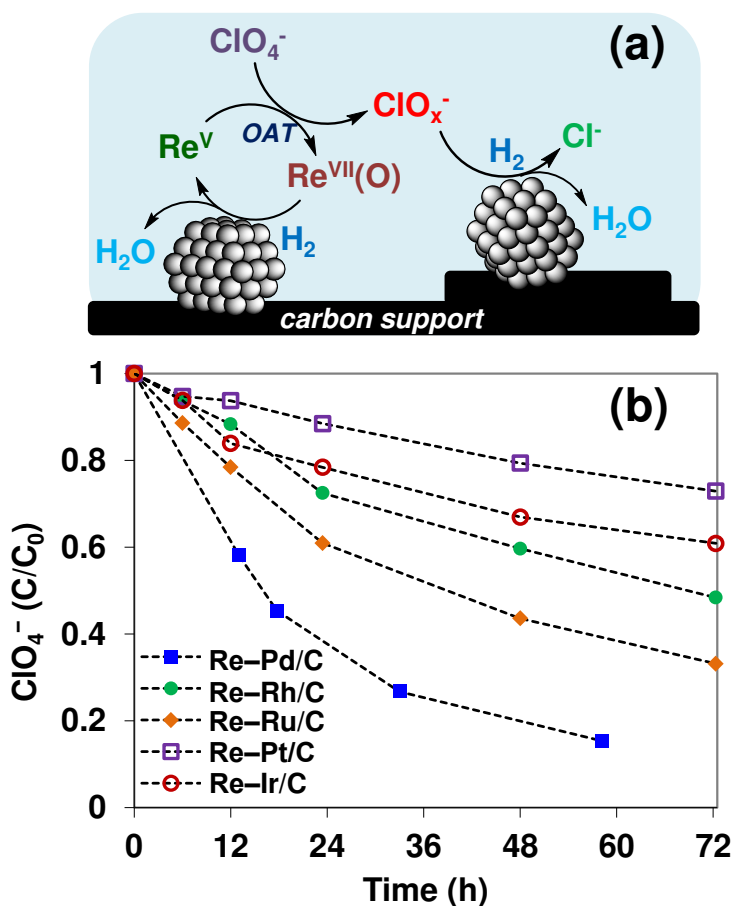
Figure 2.3 (a) Mechanisms for Re−M/C catalyst reactions with ClO_4^- and ClO_x^- intermediates (x = 3, 2, or 1); adapted from Refs [50, 51]. (b) Reduction of 5 mM ClO_4^- with 2 g L^{-1} Re−M/C (5 wt% Re, 5 wt% M) bimetallic catalysts.

interpretation of this trend is unclear at this time. This is complicated by the fact that previous work shows that the rate of ClO_4^- reduction by OAT reactions is more heavily influenced by the speciation of the immobilized Re species than the identity of the hydrogenation metal.[53, 54] Nevertheless, these results demonstrate that all five hydrogenation metals are capable of sustaining the redox turnover of surface Re species (Eqs. 2.6 and 2.7) required to catalyze the OAT reaction with ClO_4^- (turn over number, TON = 38 for each Re atom to fully reduce 5 mM ClO_4^- to Cl^- with the catalyst loadings used in the experiment).

2.4.6   Mechanistic insights from metal and AO_3^- reactivity cross comparisons

Comparison of observed reactivity trends among the platinum group metals and trioxyanion substrates (AO_3^-) reveals new insights on the controlling reaction mechanisms. First, since the optimum metals for the reduction of BrO_3^- (Rh at pH 7.2) and ClO_3^- (Ru at pH 7.2) differ, the oxyanion substrates should have direct interactions with metal nanoparticle surfaces to undergo reduction (Figure 2.4a). If the oxyanions mainly react with dissociated atomic hydrogen that is "spilled" away from the metal nanoparticles (Figure 2.4b),[55, 56] the order of catalytic activity for the five metals toward the three oxyanions may be expected to be more

similar. However, the measured activity order is Rh > Ir > Pt ~ Pd ~ Ru for BrO_3^- reduction at pH 7.2, and Ru >> Rh > Ir > Pt > Pd for ClO_3^- reduction at pH 7.2 (Table 2.2). In addition, we note that the observed activity trends are different from those previously report by Restivo *et al*.,[34] where the M/C catalysts were prepared in the researchers' own laboratory and exhibited much lower BrO_3^- reduction activity (e.g., > 15 min was required to completely reduce 0.078 mM BrO_3^- by 2 g L^{-1} of 1 wt% M/C catalysts) than our experimental results (e.g., 5 min to completely reduce 1.0 mM BrO_3^- by 0.1 g L^{-1} 5 wt% Rh/C). We note that the differences of BrO_3^- concentration and catalyst loading have overweighed the effect of metal loading.
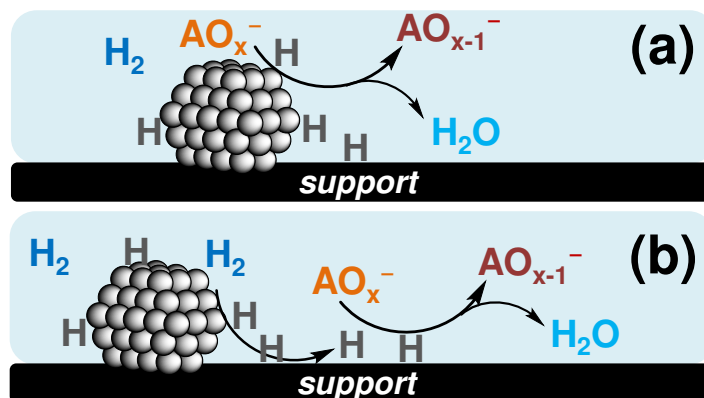
Figure 2.4 Mechanism illustrations of (a) the reduction of oxyanion substrates (AO_x^-) requiring direct interaction with the hydrogenation metal nanoparticles; (b) the reaction between AO_x^- and spilled over atomic hydrogen at the catalyst support surface away from the hydrogenation metal nanoparticles.

Explanation of the discrepancies of catalyst activity in different reports, if necessary, would require substantial amount of catalyst characterization and comparison. It is probable that critical catalytic properties of individual metals might have not be revealed when using a uniform catalyst preparation recipe for all metals (i.e., the recipes were not optimized for individual metal) by the Pereira and Neves team.

Nevertheless, results suggest that the mechanistic interpretation, which might be used as design rationale for future catalyst development work, should be considered with caution. Restivo *et al*. observed Pt and Ru to be the most active metals for BrO_3^- reduction, and this observation was correlated with the hydrogen chemisorption energy on each metal using the Sabatier principle.[34] However, based on the activity of Rh and Ir in the current study, we propose that hydrogen chemisorption energy might not necessarily be the key parameter controlling reactivity of different metals with BrO_3^-, and that the interaction between oxyanion substrates and different metal surfaces should also be considered.

Second, the pH responses of the five metals are also different. For BrO_3^- reduction, the pH responses of Rh and Ru contrast those of Pd, Pt and Ir (Table 2.2). Also, the same Rh/C catalyst exhibits differing pH dependence for BrO_3^- reduction compared to ClO_3^- and NO_3^- reduction (Figure 2.5, activity presented in apparent rate constants normalized by the mass of M/C catalysts), even though the three oxyanions carry the same -1 charge in solutions between
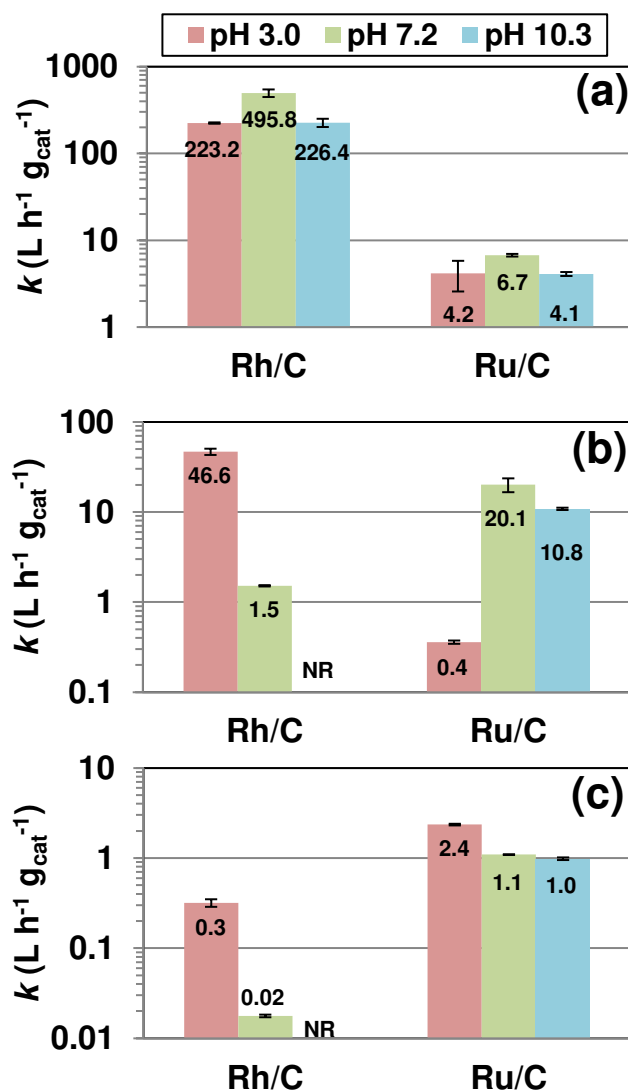
Figure 2.5 Catalyst loading normalized rate constants at different pH for the reduction of 1 mM (a) BrO_3^-, (b) ClO_3^- and (c) NO_3^- with Rh/C and Ru/C catalysts. Error bars represent replicate-averaged 95% confidence intervals. "NR" indicates no reaction observed within the reaction period monitored.

pH 3.0 and 10.3. In comparison, Ru/C catalyst did not show a simple trend of pH dependence. Zeta potentials of Rh/C and Ru/C under variable pH (with a H_2 atmosphere[20, 52]) were measured and results are shown in Figure 2.6. Although the zeta potentials of both catalysts are significantly increased when the pH decreases from 7.2 to 3.0, the BrO_3^- reduction by Rh/C and Ru/C (Figure 2.6a) as well as the ClO_3^- reduction by Ru/C (Figure 2.6b) are not accelerated. Previous reports attribute slower rates of BrO_3^- reduction by Pd catalysts at higher pH to increased negative surface charge and the resulting unfavorable electrostatic interactions between the surface and the negatively charged oxyanions.[20, 57] Here, results demonstrate that a more positively charged support at lower pH does not necessarily increase rates of oxyanion reduction for all M/C. Hence, the intrinsic reactivity of metals may outweigh the effects of catalyst surface charge. Therefore, the priority of designing an oxyanion reduction catalyst should consider the selection of active metal according to the characteristics of oxyanion substrates and reaction conditions (e.g., solution pH).
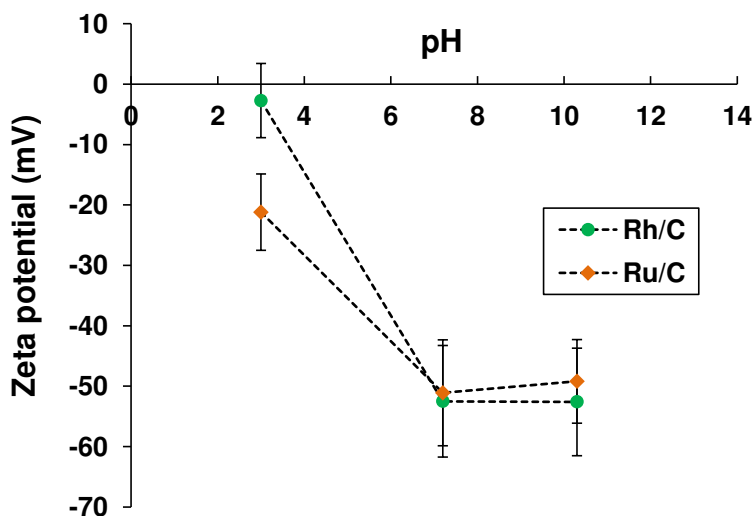
Figure 2.6 Influence of pH on the zeta potential of 0.5 g L^{-1} Rh/C and Ru/C catalysts in H_2-saturated aqueous suspension at 22 °C.

2.4.7 Outlook in catalyst development and application

In this study, four platinum group metals, which have been largely overlooked during the development of Pd-based water treatment catalysts, exhibit much higher or at least similar performance in comparison to Pd, in terms of catalytic turnover frequency, pH dependence, and oxyanion substrate scope. Specifically, Ru shows outstanding activity for ClO_3^- and NO_3^- reduction over a wide pH range, and the price of Ru is more than an order of magnitude lower than the other four metals (Table A.1 in Appendix A). Thus, lower cost and more sustainable reductive catalytic technologies[15, 16] may be achieved by developing Ru-based multi-functional materials. Moreover, our research group has developed highly stable ClO_4^- reduction catalysts based on Rh rather than Pd, because the former could rapidly scavenge ClO_x^- intermediates that can deactivate Re complex reaction sites.[39, 54] Results from this study are expected to initiate the development of new catalysts for a variety of water treatment scenarios.

Various factors such as size and morphology of both the metal nanoparticles and the support materials can also influence the reactivity of platinum group metals,[19, 57] but the effects are generally less pronounced compared to the effects of metal identity (e.g., Pd versus Rh in ClO_3^- reduction, or Pd versus Ru in NO_3^- reduction) as demonstrated in this study. Computational studies[19, 58] are also needed to provide detailed theoretical insights into these metal-specific effects and metal-substrate interactions. We emphasize that research priority should be given to further examining novel activity of these previously overlooked metals in water treatment applications, such as (1) exploring multi-functional activities in treating various emerging and challenging contaminants (e.g., nitro,[59] fluoro,[40-43] and polychloro[60, 61] compounds), and (2) rational development of catalyst formulation and engineering processes to apply these metals for practical water treatment.

2.5 Conclusions

Four platinum group metals (Ru, Rh, Ir, and Pt), largely overlooked in the development of water treatment catalysts compared to Pd, are shown here to exhibit favorable reactivity with aqueous bromate, chlorate, nitrate and perchlorate at ambient conditions. Specifically, Rh and Ru show significant advantages over Pd in terms of catalytic turnover frequency, pH dependence, oxyanion substrate scope, or cost. Cross comparison of multiple metals and tri-oxyanion substrates suggest that some previous interpretations of the pH influence on catalyst reactivity should be revisited. The chemical nature of each metal element is a key factor determining the catalyst activity and adaptability to different water treatment conditions. We recommend that rational selection of metals could be one of the current priorities in the development of water treatment catalysts.

2.6 References

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CHAPTER 3

HYDROGENATION OF AQUEOUS NITRATE AND NITRITE WITH RUTHENIUM CATALYSTS

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3.1   Abstract

Historically, development of catalysts for treatment of nitrate-contaminated water has focused on supported Pd-based catalysts, but high costs of the Pd present a barrier to commercialization. As part of an effort to develop lower cost hydrogenation catalysts for water treatment applications, we investigated catalysts incorporating Ru with lower cost. Pseudo-first-order rate constants and turnover frequencies were determined for carbon- and alumina-supported Ru and demonstrated Ru's high activity for hydrogenation of nitrate at ambient temperature and H_2 pressure. *Ex situ* gas pretreatment of the catalysts was found to enhance nitrate reduction activity by removing catalyst surface contaminants and exposing highly reducible surface Ru oxides. Ru reduces nitrate selectively to ammonium, and no aqueous nitrite intermediate is observed during reactions. In contrast, reactions initiated with nitrite yield a mixture of two endproducts, with selectivity shifting from ammonium towards N_2 at increasing

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initial aqueous nitrite concentrations. Experimental observation and Density Functional Theory calculations together support a reaction mechanism wherein sequential hydrogenation of nitrate to nitrite and NO is followed by parallel pathways involving the adsorbed NO: (1) sequential hydrogenation to ammonium, and (2) N-N coupling with aqueous nitrite followed by hydrogenation to the detected N_2O intermediate and N_2 endproduct. These findings open the door to development of alternative catalysts for purifying and recovering nutrients from nitrate-contaminated water sources, and insights into the controlling surface reaction mechanisms can guide rational design efforts aimed at increasing activity and tuning endproduct selectivity.

3.2   Introduction

Nitrate contamination of drinking water sources is among the greatest public health threats around the world.[1] Nitrate concentrations exceeding health-based standards are routinely detected in drinking water sources due to excess fertilizer applications and release of incompletely treated industrial and domestic wastewater.[2-4] The growing contamination of drinking water sources raises health concerns because nitrate can be transformed into hazardous chemicals, including nitrite, which causes methemoglobinemia (i.e., blue baby syndrome), and potentially carcinogenic nitrosamines.[5, 6] As a result, there is great interest in the development of efficient, robust and low-cost technologies for treating nitrate-contaminated water.

Several technologies are available to separate nitrate from water, including ion exchange,[7, 8] high pressure membrane filtration,[9] and electrodialysis,[10] and have demonstrated their effectiveness in full-scale practice.[2, 11] The principal drawback of these systems is the production of a nitrate concentrate stream that requires further treatment before disposal.[12, 13] Biological denitrification is widely used for the treatment of municipal and industrial wastewater, but concerns about pathogen introduction, the need for costly organic carbon amendments and

potential residuals, and biological sludge production have limited application for drinking water treatment.[14, 15] More recently, chemical reduction of nitrate has been increasingly explored. Zerovalent metals, including iron,[16] aluminum,[17] and magnesium,[18] stoichiometrically couple nitrate reduction with metal corrosion, but reactions are hindered by the formation of oxide surface coatings, and the need to constantly replenish the metals as reducing equivalents are consumed creates operational challenges.

As an alternative to stoichiometric metal reductants, our team and others have been investigating the application of metal hydrogenation catalysts that couple nitrate reduction with H_2 oxidation.[7, 19-23] Nitrate can be transformed into two endproducts with different H_2 and acidity requirements:

$$NO_3^- + 2.5H_2 + H^+ \rightarrow 0.5N_2 + 3H_2O \qquad (3.1)$$

$$NO_3^- + 4H_2 + 2H^+ \rightarrow NH_4^+ + 3H_2O \qquad (3.2)$$

Because the metals are acting as catalysts rather than stoichiometric reactants, they are not consumed in the process or generate a secondary solid waste stream that requires disposal. H_2 is an inexpensive electron donor that has lower life cycle environmental impacts than organic electron donors applied in most biological denitrification processes.[24] To date, most work has focused on the development of nitrate and nitrite treatment processes employing supported Pd-based catalysts.[13, 25, 26] Pd catalysts are highly effective in converting nitrite, the first daughter product of nitrate reduction, to harmless N_2 gas at an incomparable rate,[27-29] but monometallic Pd catalysts show little reactivity with nitrate.[30, 31] Deposition of a second "promoter" metal (e.g., Cu, In, Sn) together with Pd is typically required to facilitate reduction of nitrate to nitrite.[23, 31, 32] A large body of literature has reported on aqueous nitrate reduction with Pd-based bimetallic catalysts,[20, 30, 31, 33-37] and our current understanding of metal-catalyzed nitrate hydrogenation

mechanisms has been limited to reactions occurring with these materials. The prevailing reaction pathway follows a two-step process depicted in Figure 3.1: (1) hydrogenation of nitrate to nitrite on bimetallic clusters followed by (2) further hydrogenation of nitrite on Pd sites to a mixture of N_2 and ammonium stable endproducts, the net processes being reflected by Eqs. (3.1-3.2).[22, 35, 38-40]
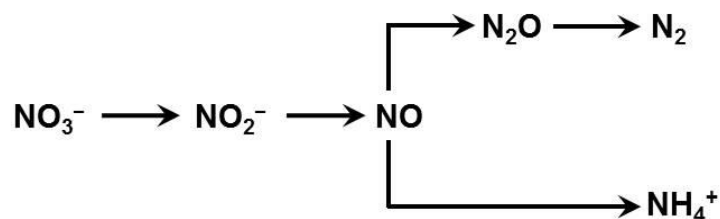
Figure 3.1 Nitrate hydrogenation pathway on Pd-based bimetallic catalysts.

The proposed sequential reduction pathway is supported by the observation of nitrite as a transient reaction intermediate,[23, 33] increasing with pH as the rate of Pd-catalyzed nitrite reduction decreases,[39, 41] and isotope labeling experiments showing Pd-catalyzed reduction of NO to the same mixture of endproducts and selective conversion of N_2O to N_2.[22] The distribution of endproducts, presumed to be controlled by the Pd-catalyzed reactions of nitrite or its daughter products (e.g., adsorbed NO), has been reported to vary with catalyst composition,[31] metal nanoparticle size,[42] support,[43] and solution pH.[44]

Although years of effort have been invested in improving the activity, endproduct selectivity, and long-term stability of Pd-based bimetallic catalysts[31, 45] (and to a lesser extent Pt-based catalysts,[36, 46]) deployment of practical catalytic treatment systems remains limited, in large part, due to high costs of Pd.[47] Precious metal-free catalysts based on Ni have been explored,[15, 48, 49] but instability in aqueous matrices,[50] and serious concerns about the associated

leaching of dissolved Ni^{2+}[51] and the pyrophoric nature of highly active Raney Ni[52] have limited further development efforts.

As a result of the low nitrate and nitrite reduction activity reported in early catalyst screening studies,[27, 28] Ru hydrogenation catalysts have been largely overlooked for such applications. However, a renewed examination of the application of Ru-based catalysts is warranted because of the historically much lower price of Ru in comparison to Pd and Pt[47] as well as the metal's documented catalytic activity for a diverse range of reactions, including hydrogenation, hydrodeoxygenation and hydrodechlorination reactions.[53, 54] In addition, work on electrochemical reduction of nitrate (in acidic media) has shown that Ru electrodes exhibit higher activity than Pt, Pd and Ir electrodes.[55] After recently screening a range of metal catalysts as alternatives to Pd for reduction of oxyanion pollutants,[56] this contribution focuses on a renewed evaluation of the kinetics and mechanisms of nitrate and nitrite reduction by supported Ru catalysts. Reaction kinetics, product distribution analysis, and catalyst characterization studies are combined with Density Functional Theory (DFT) calculations to improve our understanding of interaction between nitrate (and nitrite) and Ru metal surfaces and elucidate the origin of endproduct selectivity.

3.3   Materials and methods

3.3.1   Catalysts

A full listing of chemical reagents is provided in Section B.1.1 in Appendix B. Ru and Pd catalysts immobilized on carbon and alumina supports (nominal 5 wt% metal) were purchased from Sigma-Aldrich. Unless otherwise noted, the as-received Ru and Pd catalysts were pretreated *ex situ* in flowing H_2 at 350 °C for 2 h prior to use in aqueous oxyanion reduction experiments. The only exception to this was for experiments specifically examining the effects of

different *ex situ* pretreatments (see Section 3.4.2), wherein the as-received catalysts (no pretreatment), catalysts pretreated *ex situ* in flowing N_2 at 350 °C for 2 h, and catalysts pretreated *ex situ* in flowing H_2 as mentioned above were compared. No precautions were taken following pretreatment to avoid surface passivation upon exposure to air. Bimetallic Pd-Cu/C, Ru-Cu/C, and Ru-In/C catalysts were prepared by incipient wetness impregnation[57] of 1 wt% of Cu (as $Cu(NO_3)_2 \cdot 3H_2O$) or In (as $In(NO_3)_3 \cdot 3H_2O$) on as-received commercial Pd/C and Ru/C, respectively, followed by air drying at 110 °C for 12 h and H_2 at 350 °C for 2 h.

Catalysts were extensively characterized, including metal content (inductively coupled plasma-optical emission spectrometry, ICP-OES), specific surface area and average pore diameter of the support materials (N_2 physisorption), metal dispersion (the percentage of Ru or Pd atoms present on the clean surface of the immobilized metal nanoparticles, CO chemisorption), active surface (the percentage of Ru or Pd atoms accessible to reactants under simulated *in situ* conditions, CO chemisorption), morphology and size of the metal nanoparticles (transmission electron microscopy and high-angle annular dark-field-scanning transmission electron microscopy, TEM and HAADF-STEM), Ru reducibility (H_2 temperature-programmed reduction, H_2 TPR), and long-range structural order (X-ray diffraction, XRD). Details of each methodology are provided in Section B.1.2 in Appendix B.

3.3.2 Nitrate and nitrite reduction kinetics

Aqueous nitrate and nitrite reduction kinetics were measured in an open semi-batch system under continuous H_2 sparging (1 atm, 40 mL min^{-1}) at constant temperature (25 ± 0.5 °C). A 250 mL three-neck reactor was filled with 150 mL deionized water and predetermined mass of catalyst. The suspension was sonicated for 5 min and sparged with H_2 gas for 30 min before introducing a small volume of $NaNO_3$ or $NaNO_2$ stock solution to initiate the reaction. Reaction

progress was monitored by periodic collection of suspension aliquots (1.5 mL) that were immediately filtered (0.22 µm cellulose acetate) to remove catalyst particles and quench reactions prior to analysis by ion chromatography (NO_3^- and NO_2^-) and colorimetric assay (NH_4^+). The suspension was mixed by a Teflon-coated magnetic stir bar at 700 rpm. Solution pH was maintained by HCl addition from an automatic pH-stat (Radiometer TitraLab 854). Catalyst activity was assessed by quantifying initial mass-normalized pseudo-first-order rate constants (k_0, L $g_{Ru/Pd}^{-1}$ min^{-1}) and turnover frequencies (TOF_0, min^{-1}), defined as the number of nitrate or nitrite ions reduced per active surface site per minute. The active surface was estimated from CO chemisorption measurement using an assumed 1:1 CO:Metal adsorption stoichiometry.[58, 59] Additional details of the procedures for kinetics parameter calculations and aqueous analytical measurements are provided in Sections B.1.3 and B.1.4 in Appendix B. A catalyst re-use experiment was carried out to evaluate the stability of Ru/C. After a semi-batch reaction was complete, the catalyst solid was collected on a filter (glass fiber filter; EMD Millipore), washed with deionized water several times, and vacuum dried at 65 °C overnight before re-suspending in water for the subsequent semi-batch reaction. The catalyst was also re-characterized after completion of the re-use experiment.

3.3.3 Isotope labeling experiments

Nitrogen mass balances and endproduct distributions were quantified using closed-bottle batch experiments with the aid of ^{15}N-labeled nitrate and nitrite salts to avoid the interference from atmospheric $^{14}N_2$ during mass spectrometry measurement of the N_2 endproduct.[22] A 160 mL serum bottle with 75 mL of an organic buffer, 4-morpholineethanesulfonic acid (MES) (pH 5.5, 40 mM), a predetermined mass of catalyst, and a Teflon-coated magnetic stir bar was sealed by a 1.0 cm-thick rubber stopper held in place by an Al crimp cap. Experiments were conducted

at ambient temperature (21 ± 1 °C) and suspensions were mixed in the same manner as the semi-batch experiments. The reactor was sparged with H_2 for 30 min to saturate the headspace and solution before introducing the target oxyanion pollutant. A H_2-sparged stock solution of $Na^{15}NO_3$ or $Na^{15}NO_2$ was then added to the reactor to initiate the reaction, and 1.5 mL aqueous aliquots were withdrawn by syringe through the gas-tight septa to monitor disappearance of the parent reactant and the evolution of aqueous intermediates and products. Headspace samples (0.1 mL) were collected separately and immediately analyzed for labeled gaseous intermediates and products (^{15}NO, $^{15}N_2O$, and $^{15}N_2$) by gas chromatography-mass spectrometry (GC-MS, details in Section B.1.4 in Appendix B). Headspace gases were assumed to be maintained in equilibrium with the aqueous phase at all times,[60] which was supported by good nitrogen mass balance closure. Analyte values in these experiments are reported in moles of nitrogen because products include both liquid and gas species as well as both mono- and diatomic nitrogen species. The total mass of H_2 initially added to the sealed batch reactor (~3.4 mmol) was in significant excess of the stoichiometric requirement for the complete reduction of the added NO_3^- to NH_4^+ (~0.5 mmol).

3.3.4 Computational methods

DFT calculations of N-containing species associated with Ru metal surfaces were performed with the Gaussian 09 suite of programs.[61] A Ru_{18} metal cluster structure was used to model Ru catalysts based on the work of Aguilera-Granja *et al*.[62] and Zhang *et al*.[63] It was shown that Ru and Rh clusters with fewer than 20 atoms adopt simple cubic or distorted cubic structure. Geometry optimizations of Ru clusters were completed at the PBE0[64] level of theory with the Lanl2DZ basis set.[65, 66] The core electrons of Ru atoms were modeled using the SDD effective core pseudo-potential.[65, 67] The PBE0 functional was shown to be a reliable method in predicting

both the properties and reactions involved with transition metals and metal clusters[68], including

Ru, with accuracies approaching or exceeding other functionals commonly utilized in solid state

systems.[69]

Small molecule (i.e., nitrate, nitrite, and other reacting species) adsorption to the metal

clusters were optimized at the PBE0/Lanl2DZ(Ru)/6-31+G(d,p)(H, N, O) level of theory. The

geometry optimization of small molecules was performed with the Ru cluster fixed.

Thermodynamic barriers were calculated from the bottom of the well energies, as

thermodynamic corrections would be an unnecessary addition of error due to the frozen bond

constraints given to the metal atom centers. The integral equation formalism polarizable

continuum model (IEF-PCM)[70] was used to implicitly model the aqueous environment and was

present in all optimizations and single point energy calculations. To correct for spin

contamination for unpaired electron intermediates, single point energies utilizing a restricted

open shell (RO) wavefunction were calculated at the ROPBE0/Lanl2DZ(Ru)/6-31+G(d,p)(H, N,

O) level of theory. When multiple conformations of adsorbed N-containing species were possible,

the complexes with the lowest energy were chosen for the calculation of reaction energies.

3.4   Results and Discussion

3.4.1   Catalytic nitrate reduction

Figure 3.2 shows the catalytic reduction of aqueous nitrate on Ru/C in comparison to

monometallic Pd/C and bimetallic Pd-Cu/C. In contrast to an earlier report of limited nitrate

reactivity with Ru catalysts,[28] these experiments demonstrate that Ru is an effective catalyst,

exhibiting much greater activity than monometallic Pd/C of the same mass loading and similar

activity to Pd/C after immobilization of 1 wt% Cu as secondary promoter metal. For all three

catalysts shown in Figure 3.2, nitrate reduction kinetics follow a pseudo-first-order rate law over

at least the first reaction half-life, and model fits of the data shown yield Ru- and Pd-mass-normalized pseudo-first-order rate constants of 4.13 ± 0.30 L g_{Ru}^{-1} min^{-1}, 0.46 ± 0.08 L g_{Pd}^{-1} min^{-1}, and 4.18 ± 0.01 L g_{Pd}^{-1} min^{-1} for Ru/C, Pd/C, and Pd-Cu/C catalysts, respectively.

The rate constants are calculated using the metal loading reported in Table 3.1. Control experiments conducted under continuous N$_2$ sparging (catalyst suspensions sparged with H$_2$ for 30 min followed by N$_2$ for another 60 min to displace H$_2$ before introducing nitrate to the reactor) show negligible loss of nitrate, demonstrating minimal adsorption onto the catalyst supports. Since the catalysts were subjected to the same *in situ* H$_2$ pre-reduction step before switching to N$_2$ sparging, this observation also indicates negligible direct reduction of nitrate by the metallic Ru or Pd phases. Initial rates of nitrate reduction vary linearly with catalyst loading between 0 and 0.5 g L^{-1} Ru/C (Figure B.2 in Appendix B), indicating that catalyst suspensions were well mixed and under the studied conditions. The estimated Weisz-Prater parameter (C_{wp})
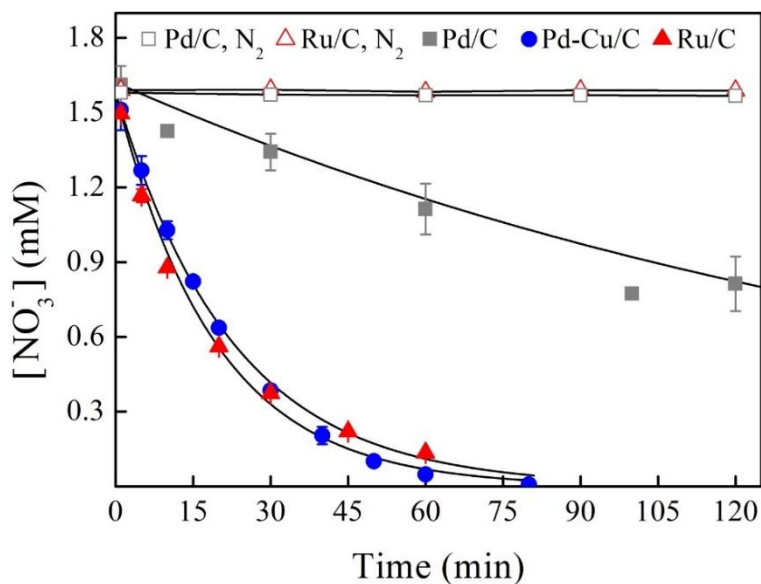
Figure 3.2 Measured reaction timecourses for nitrate reduction and first-order model fits on 5 wt% Ru/C, 5 wt% Pd/C, and 5 wt% Pd-1 wt% Cu/C in the semi-batch reactor system (0.2 g L^{-1} catalyst, [NO$_3^-$]$_0$ = 1.6 mM, 1 atm H$_2$ continuous sparging except in control experiments where 1 atm N$_2$ continuous sparging was used, pH 5.0 maintained by pH stat, 25 ± 0.5 °C). Error bars represent standard deviations of triplicate reactions.

(Section B.2.1 in Appendix B) is <<1, indicating that the internal mass transfer within the porous catalyst support particles is also not rate limiting. Ru/C exhibited good stability in batch re-use experiments, with activity decreasing <5% after each run (Figure B.3 in Appendix B). Dissolved Ru measured in the supernatant of catalyst suspensions was below 1 ppb, demonstrating negligible leaching of the active metal. Electron microscopy of the catalyst collected following repeated re-use shows no agglomeration or growth of Ru nanoparticles (Figure 3.3a and b). The small drop in activity observed between runs is speculated to be caused by material loss during the filtration recovery protocol used between runs. Immobilization of secondary promoter metals (1 wt% Cu and In) that have been reported to enhance nitrate reduction activity for Pd catalysts did not enhance Ru/C reactions with nitrate (data not shown).

Reductive transformation of nitrate, rather than adsorption or other transformation process, is also confirmed by the good nitrogen mass balance closure (Figure 3.4a) observed using closed-bottle batch experiments with the aid of a ^{15}N-labeled nitrate salt that eliminated potential artifacts from atmospheric contamination during analysis of N_2. For Ru/C, nitrate is converted selectively to ammonium without producing any detectable [15]N_2 by GC-MS analysis, and none of the transient aqueous or gaseous intermediates typically observed for Pd-based catalysts (nitrite and N_2O)[39, 71] are detected.

The effect of solution pH on nitrate reactions with Ru/C was evaluated in the open semi-batch systems using HCl/NaOH to maintain pH (Figure B.4 in Appendix B). Ru-mass-normalized pseudo-first-order rate constants are relatively constant between pH 5-8, but decrease significantly at lower and higher pH conditions. Since gaseous nitrogen species cannot be measured in the open semi-batch reactors sparged continuously with H_2, a stringent mass balance analysis of endproducts was not feasible. However, ammonium product yields reached ≥90% of

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Table 3.1 Properties of catalysts used for nitrate activity test.

Catalyst	BET surface area (m^2 g^{-1})	Total pore volume[a] (cm^3 g^{-1})	Average pore diameter[b] (nm)	Metal loading (wt%)	Metal dispersion (%)	Active surface (%)	Chemisorption particle size (nm)	TEM particle size (nm)	TOF$_0$ (min^{-1})[c]
Ru/C	859.7	0.74	3.46	5.38[d]	38	32	3.5	2.2 ± 0.8	2.1 ± 0.2
Ru/Al$_2$O$_3$	93.1	0.36	15.34	5[e]	15	9	8.8	8.1 ± 3.0	2.4 ± 0.5
Pd/C	856.9	0.72	3.35	6.24[d]	17	19	6.5	4.1 ± 2.2	0.42 ± 0.07
Pd/Al$_2$O$_3$	98.4	0.24	9.69	5.85[d]	16	15	6.9	4.2 ± 1.1	NR[f]

[a]Adsorption total pore volume at $P/P_0 = 0.97$. [b]Calculated from total pore volume and BET surface area. [c]Calculated based on active surface. [d]Measured by ICP-OES analysis. [e]Nominal value provided by supplier. [f]No reaction observed.
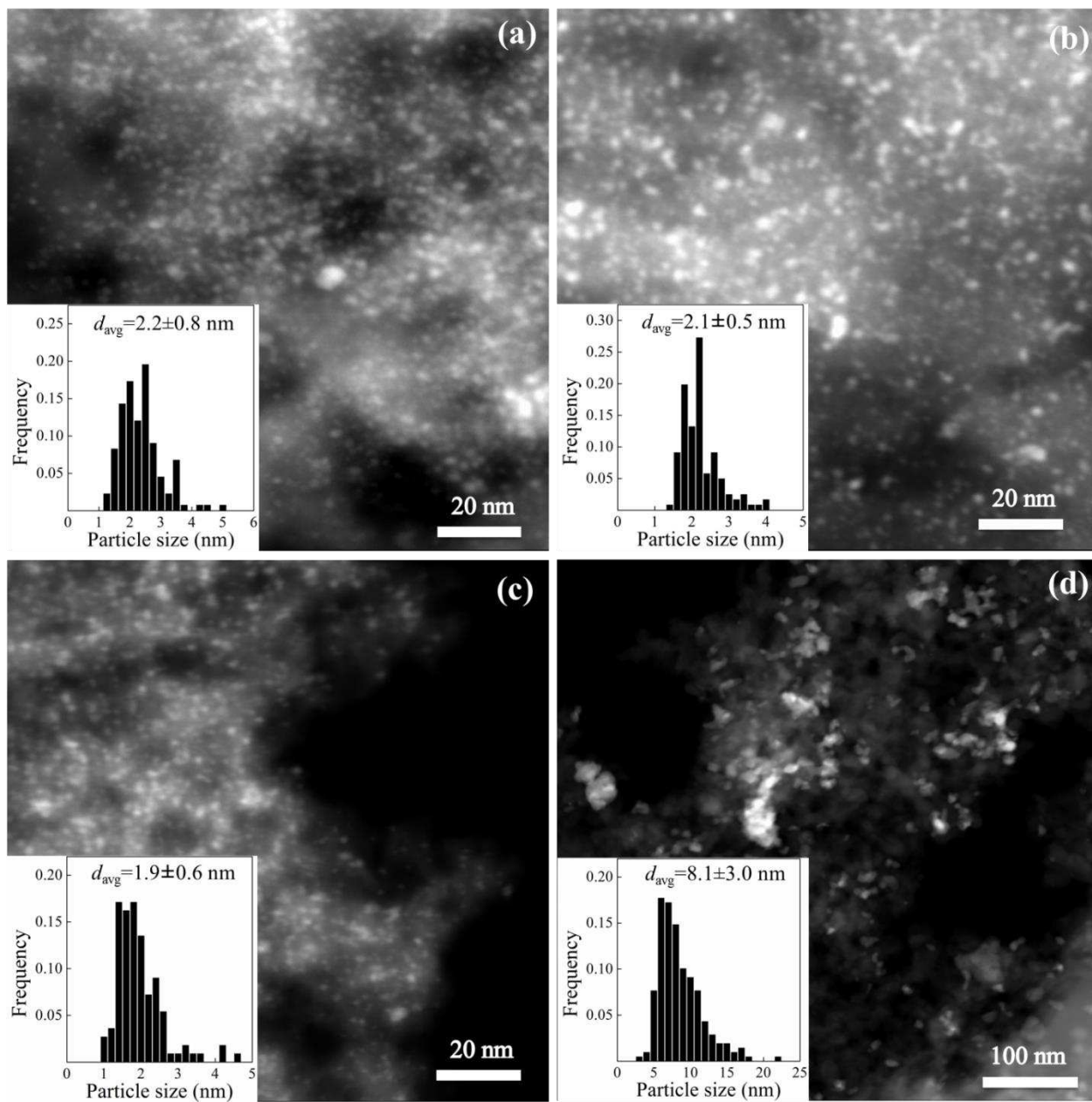
Figure 3.3 HAADF-STEM images of (a) *ex situ* H_2 pretreated Ru/C, (b) Ru/C after re-use experiment, (c) as-received Ru/C and (d) *ex situ* H_2 pretreated Ru/Al$_2$O$_3$. The insets show Ru particle size distributions.

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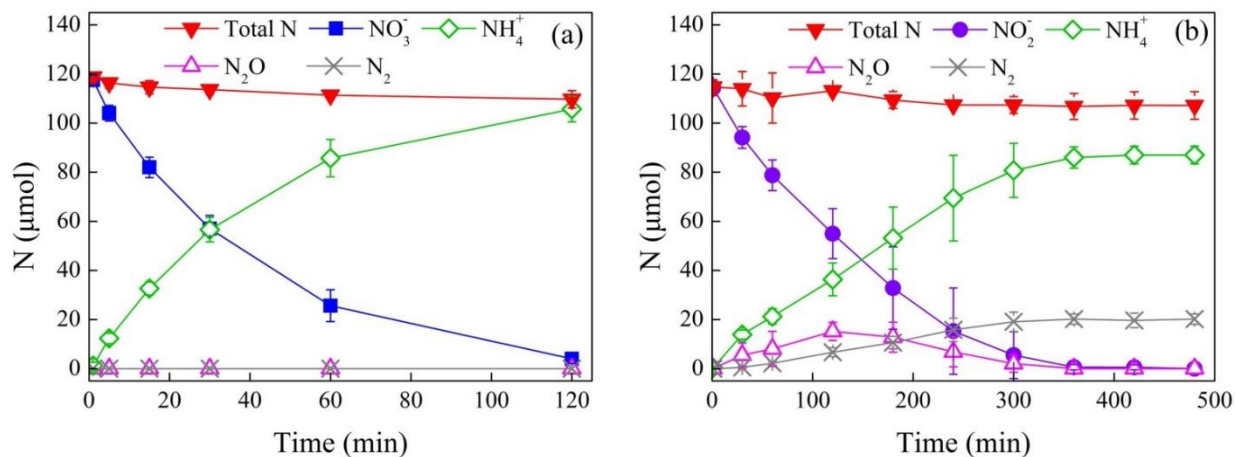
Figure 3.4 Timecourses showing aqueous and gaseous intermediates and products during Ru/C-catalyzed reduction of ^{15}N-labeled (a) nitrate and (b) nitrite monitored in closed-bottle batch systems (0.2 g L^{-1} catalyst, [$^{15}NO_3^-$]$_0$ or [$^{15}NO_2^-$]$_0$ = 1.6 mM , initially 1 atm H$_2$, pH 5.5 buffered by 40 mM MES, 21 ± 1 °C). Error bars represent standard deviations of triplicate reactions (smaller than symbol if not visible).

the initial nitrate concentrations for all pH conditions, consistent with the high selectivity measured in the closed reactor experiment conducted at pH 5.5 using ^{15}N-labeled species (Figure 3.4a).

Comparison between metal dispersion and active surface in Table 3.1 suggests that 30 min of H$_2$ treatment at 25 °C is sufficient to re-reduce a large fraction of any surface oxides that might form upon air passivation of *ex situ* H$_2$ pretreated catalysts. Despite the heterogeneity in particle morphology (Figure 3.3 and Figure B.5 in Appendix B) and an assumed 1:1 CO:Metal adsorption stoichiometry for all catalysts irrespective of metal particle size and support, metal dispersion values derived from CO chemisorption analysis[72] are reasonably consistent with particle sizes observed by electron microscopy (Table 3.1). The rate constants for monometallic catalysts correspond to initial turnover frequencies (TOF$_0$) of 2.1 ± 0.2 min^{-1} for Ru/C and 0.42 ± 0.07 min^{-1} for Pd/C based on active metal surface. TOF$_0$ of nitrate reduction on Ru/C is five times greater than that of Pd/C. The higher reactivity of monometallic Ru/C than Pd/C is especially noteworthy because the Pd/C reactivity observed in Figure 3.2 is actually much

greater than that reported in earlier studies that found either no reaction with nitrate or a very low extent of reaction.[30, 31, 56, 73-75] Trawczyński *et al.*[71] calculated TOF_0 of nitrate reduction on an in-house prepared Pd/C catalyst to be ~0.03 min^{-1}, which is one order-of-magnitude lower than the TOF_0 calculated from data for Pd/C in Figure 3.2. Considering that deionized water (≥ 18 $M\Omega \cdot cm^{-1}$) was used for all experiments and known promoter metals for Pd catalyst including Cu, In, and Sn were not detected by Energy Dispersive X-ray spectroscopy analysis of Pd/C, we believe that the higher activity of Pd/C observed here is not due to promoter metal contamination from solution or surface residues present following synthesis of catalyst support.

The nature of active sites in Pd-Cu bimetallic catalysts is not well understood or characterized. Although it is technically possible to estimate surface atoms by H_2 chemisorption,[23, 76] we believe the measurement does not represent bimetallic sites and chose not to calculate the TOF_0 for nitrate reduction on Pd-Cu/C or compare the intrinsic activity between Ru and Pd-Cu bimetallic surface. However, it can be seen from Table B.1 in Appendix B that the Pd-Cu/C catalyst prepared for comparison in this study exhibits activity on a Pd mass-normalized basis that is comparable with other studies that focused in greater depth on the activity and mechanism of such bimetallic catalysts.

3.4.2   Effect of pretreatment on nitrate reduction activity

The high activity of Ru/C with nitrate observed here in comparison with earlier reports warrants further examination. Several studies have documented that the reactivity of supported metal nanoparticles is influenced by nanoparticle size and shape, chemical state, support properties and metal-support interaction, which are subject to the starting materials (support material and metal precursor), synthesis methods and activation steps.[36, 77] The present study used commercially produced catalysts to take advantage of materials with optimized industrial

production and adapted for large scale applications. However, the high reactivity with aqueous nitrate of Ru catalysts was demonstrated with the catalyst pretreated *ex situ* in flowing H_2 at 350 °C for 2 h prior to use, and the as-received Ru/C and Ru/Al$_2$O$_3$ show low or no activity. To further characterize the effects of *ex situ* pretreatment on catalyst activity, we had commercial Ru/C, Ru/Al$_2$O$_3$, Pd/C and Pd/Al$_2$O$_3$ subjected to *ex situ* heat treatment (350 °C, 2 h) in both inert gas (N_2) and reducing gas (H_2) and tested of their nitrate reduction activity. The metal mass-normalized pseudo-first-order rate constants for nitrate reduction with these materials are calculated and presented in Figure 3.5. *Ex situ* pretreatment of Ru/C, either with flowing H_2 or N_2, leads to more than a threefold increase in catalyst activity compared to the as-received catalyst. The effect of pretreatment is most pronounced for Ru/Al$_2$O$_3$, in that the catalyst is only active after pretreatment in flowing H_2. In comparison, pretreatment has no effect on the activity of Pd/C. Pd/Al$_2$O$_3$ exhibited no activity for nitrate reduction irrespective of catalyst pretreatment.
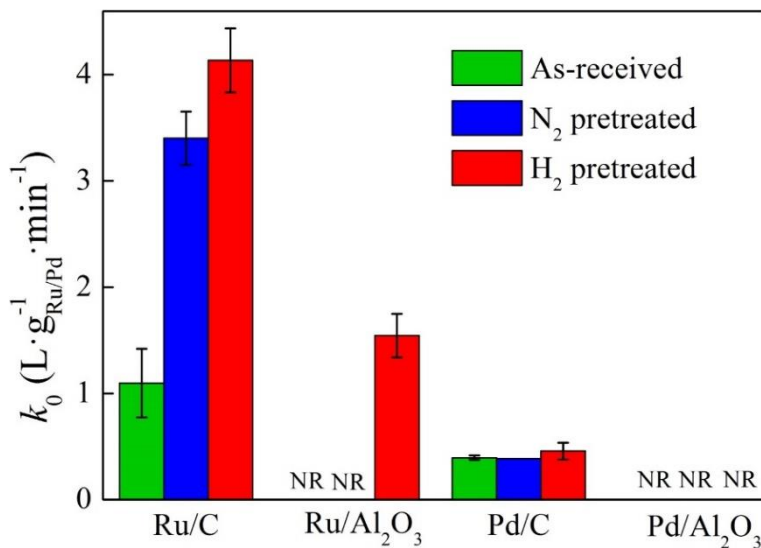
Figure 3.5 Influence of catalyst pretreatments (as-received catalyst or *ex situ* pretreated in flowing H_2 or N_2 at 350 °C for 2 h) on reactivity with aqueous nitrate (0.2 g L^{-1} catalyst with nominal 5 wt% Ru or Pd, [NO$_3^-$]$_0$ = 1.6 mM, 1 atm H_2 continuous sparging, pH 5.0 maintained by automatic pH stat, 25 ± 0.5 °C). Error bars represent standard deviations of triplicate measurements (smaller than symbol if not visible). NR = no reaction observed.

A battery of characterization analyses was conducted to rationalize the dramatic influence of *ex situ* pretreatment on Ru catalysts. XRD scan of Ru/C (Figure 3.6a) shows mainly peaks associated with crystalline carbon phases, but no significant peaks for Ru metal (ca. 44° and 38°, JCPDS card No. 06-0663) or RuO_2 (ca. 28°, 35° and 54°, JCPDS card No. 43-1027), indicating small crystal size below XRD detection limit. The XRD pattern for Ru/Al_2O_3 (Figure 3.6b) shows crystalline RuO_2 in both the as-received and *ex situ* N_2 pretreated materials, but these features disappear and new features characteristic of crystalline Ru metal appear in the H_2 pretreated Ru/Al_2O_3. For both Ru/C and Ru/Al_2O_3 catalysts, the catalyst activity (Figure 3.5) roughly correlates with the active Ru surface of catalysts (Table B.2 in Appendix B), suggesting that catalyst pretreatment increased the Ru surface area active for catalytic reaction.
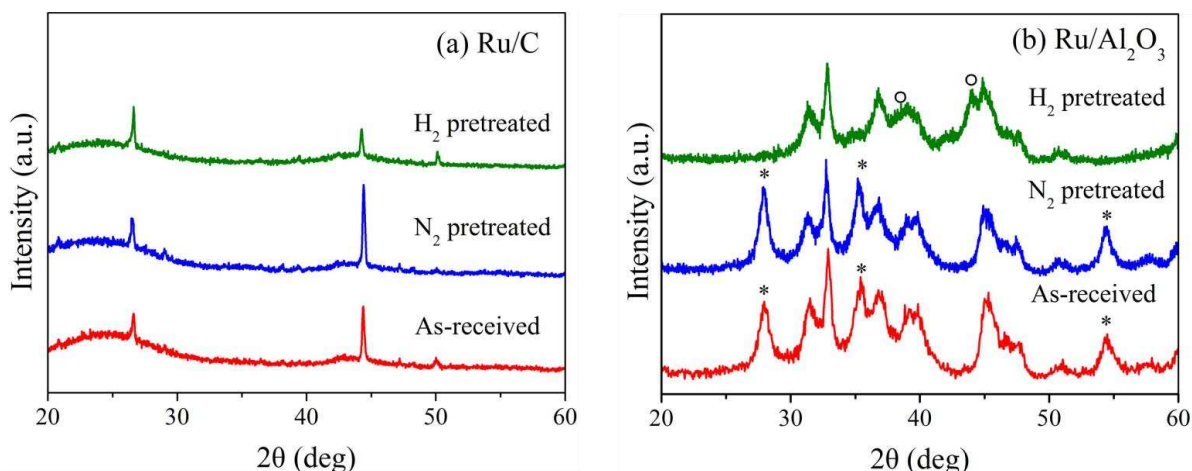
Figure 3.6 XRD patterns of (a) Ru/C and (b) Ru/Al_2O_3 collected after different *ex situ* pretreatments. Peaks assigned to Ru metal (○) and RuO_2 (*) are indicated.

Increasing surface area often results from decreased particle size, which is not the case for Ru/C in this study. The size distribution of Ru particles in the as-received Ru/C (1.9 ± 0.6 nm, Figure 3.3c) is not statistically different from that measured following the *ex situ* H_2 pretreatment process (2.2 ± 0.8 nm, Figure 3.3a). Another possibility is that the Ru catalyst surface in the as-received Ru/C is blocked by residues from synthesis, which may be partially or fully removed by

the high temperature pretreatment processes. H_2 TPR analysis provides evidence to support this hypothesis. The TPR profiles (Figure 3.7) of *ex situ* H_2- and N_2-pretreated Ru/C are similar, with a first reduction peak located between 50 and 55 °C and a second broad reduction peak above 400 °C. The reduction peak temperature of supported Ru oxides formed during catalyst calcination has been reported to vary between 65 °C and 185 °C.[78, 79] Though the temperature of the first reduction peak observed here falls below this range, the H_2 consumption quantified from the peak area (Table B.2 in Appendix B) is consistent with the theoretical stoichiometry for H_2 consumption during RuO_2 reduction[78]:

$$RuO_2 + 2H_2 \rightarrow Ru + 2H_2O \tag{3.3}$$

The Ru oxides formed upon re-oxidation of pretreated Ru upon exposure to ambient air are redox-labile, enabling re-reduction by H_2 at 25 °C. The second reduction peak is assigned to the direct reduction of aldehyde, quinone and phenol groups on the carbon support.[80] The TPR profile for as-received Ru/C is markedly different from those of *ex situ* pretreated Ru/C. A much larger H_2 consumption and a dip in the TCD signal match the features of surface species decomposition and desorption, supporting the hypothesis that the as-received catalyst surface is blocked by residues that desorb upon heat pretreatment. Temperature-programmed desorption study of as-received Ru/C and *ex situ* H_2 pretreated Ru/C in Ar provides further confirmation of surface species desorption at 47 °C for as-received Ru/C (Figure B.6 in Appendix B). Therefore, as-received Ru/C consists of highly reducible Ru oxides that are covered by surface contaminants. The *ex situ* pretreatment of Ru/C increased catalyst activity mainly by removing these surface contaminants while causing minimal effect on Ru oxides particles.

The as-received Ru/Al$_2$O$_3$ and *ex situ* N$_2$ pretreated Ru/Al$_2$O$_3$ exhibit a TPR pattern consistent with RuO$_2$ reduction reported in the literature, which is also in agreement with the
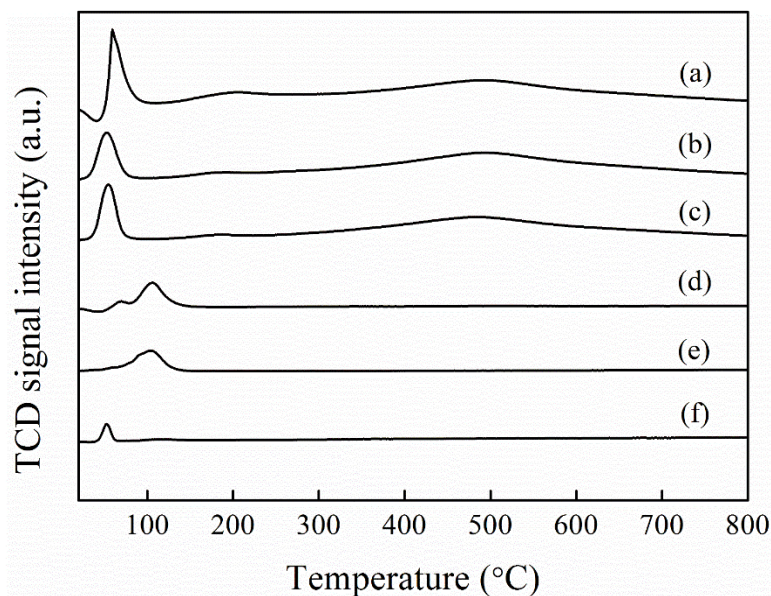
Figure 3.7 TPR profiles of (a) as-received Ru/C, (b) *ex situ* N_2 pretreated Ru/C, (c) *ex situ* H_2 pretreated Ru/C, (d) as-received Ru/Al$_2$O$_3$, (e) *ex situ* N_2 pretreated Ru/Al$_2$O$_3$, and (f) *ex situ* H_2 pretreated Ru/Al$_2$O$_3$. TCD signals are normalized with sample mass.

crystalline RuO_2 identified by XRD analysis. Although the stoichiometry for H_2 consumption of RuO_2 in these two Ru/Al$_2$O$_3$ catalysts is similar to that of RuO_2 in *ex situ* H_2- and N_2-pretreated Ru/C (Table B.2 in Appendix B), the Ru oxides on the two supports show significant differences in reducibility as evidenced by the much lower reduction peak temperature of Ru/C catalysts. Besides, the surface of RuO_2 in *ex situ* H_2- and N_2-pretreated Ru/C is easily reduced by H_2 at 25 °C, while the surface of RuO_2 in as-received Ru/Al$_2$O$_3$ and *ex situ* N_2 pretreated Ru/Al$_2$O$_3$ is not reducible with H_2 at 25 °C (Table B.2 in Appendix B). In contrast, *ex situ* H_2 pretreated Ru/Al$_2$O$_3$ shows a small H_2 consumption peak at 45 °C, similar to the highly reducible RuO_2 in *ex situ* H_2- and N_2-pretreated Ru/C and consistent with crystalline metallic Ru in *ex situ* H_2 pretreated Ru/Al$_2$O$_3$ identified by XRD analysis. Based on these observations, it can be concluded that *ex situ* H_2 pretreatment activates Ru/Al$_2$O$_3$ by reducing the crystalline RuO_2 to a metallic Ru phase, whose surface is re-oxidized upon exposure to ambient temperature air to a more redox-labile form of RuO_2 (e.g., less crystalline) that can be re-reduced by H_2 at 25 °C. A

complete re-oxidation of pretreated Ru/C compared with partial re-oxidation of H_2 pretreated Ru/Al$_2$O$_3$ is attributed to a much smaller size of Ru nanoparticles in Ru/C than in Ru/Al$_2$O$_3$. The *ex situ* N$_2$ pretreatment fails to activate Ru/Al$_2$O$_3$ due to the inability of N$_2$ to transform crystalline RuO$_2$ to redox-labile species. Therefore, it is further confirmed that redox-labile surface Ru oxides are essential to achieve good performance in catalytic nitrate reduction applications.

3.4.3 Catalytic nitrite reduction

Based on the prevailing mechanism for nitrate reduction with Pd-based catalysts, the first reduction intermediate is anticipated to be nitrite,[32, 81, 82] and the fact that no nitrite intermediate is observed when monitoring nitrate reactions (Figure 3.4a) would suggest nitrite reduction is much faster than nitrate reduction at comparable conditions (similar to observations reported for Pd catalysts under most conditions [31, 73, 83]). Compared to nitrate, reduction of nitrite is less well described by a pseudo-first-order rate law, with the reaction appearing to accelerate as nitrite concentration continues to drop after the first two half-lives (Figure 3.8a). Nevertheless, the pseudo-first-order rate constants for nitrite reduction over the first two half-lives was calculated to provide a rough measure of catalyst activity to compare with that measured for nitrate reduction under similar conditions. Surprisingly, the observed reaction kinetics for nitrite are markedly slower than for nitrate under the same conditions. The mass-normalized pseudo-first-order rate constant for nitrite reduction derived from the model fit of data in Figure 3.8a is 1.44 ± 0.15 L g$_{Ru}^{-1}$ min^{-1}, corresponding to an TOF$_0$ of 0.73 ± 0.06 min^{-1}. This value is about one third of the TOF$_0$ for nitrate measured under the same conditions (2.1 ± 0.2 min^{-1}). The lower activity of nitrite in comparison to nitrate contrasts with typical results reported for Pd-based bimetallic

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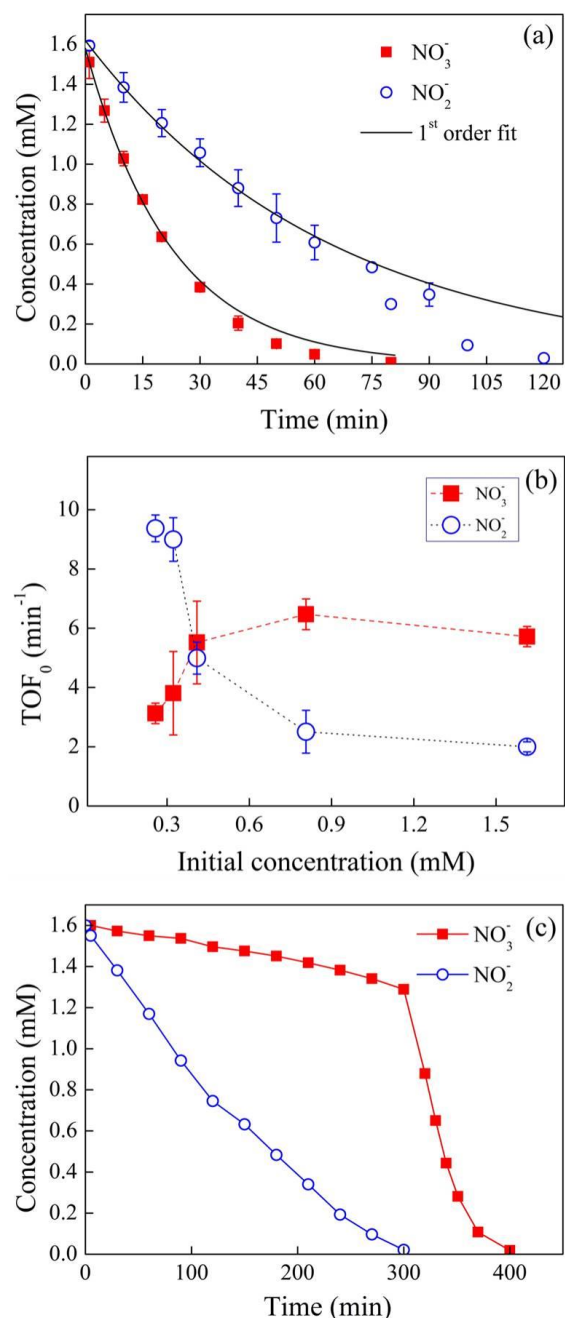
Figure 3.8 (a) Comparison of Ru/C-catalyzed nitrite reaction kinetics with nitrate reaction at standard conditions (0.2 g L^{-1} Ru/C, [NO$_3^-$]$_0$ or [NO$_2^-$]$_0$ = 1.6 mM). (b) TOF$_0$ of Ru/C-catalyzed nitrate and nitrite reduction as a function of initial concentration of the target oxyanion (0.2 g L^{-1} Ru/C). (c) Measured timecourses for the simultaneous reduction of nitrate and nitrite added to a suspension containing Ru/C (0.2 g L^{-1} catalyst, [NO$_3^-$]$_0$ = [NO$_2^-$]$_0$ = 1.6 mM). Other conditions include 1 atm H$_2$ continuous sparging, pH 5.0 maintained by automatic pH stat, and 25 ± 0.5 °C. Error bars in panels a-b represent standard deviations of triplicate measurements.

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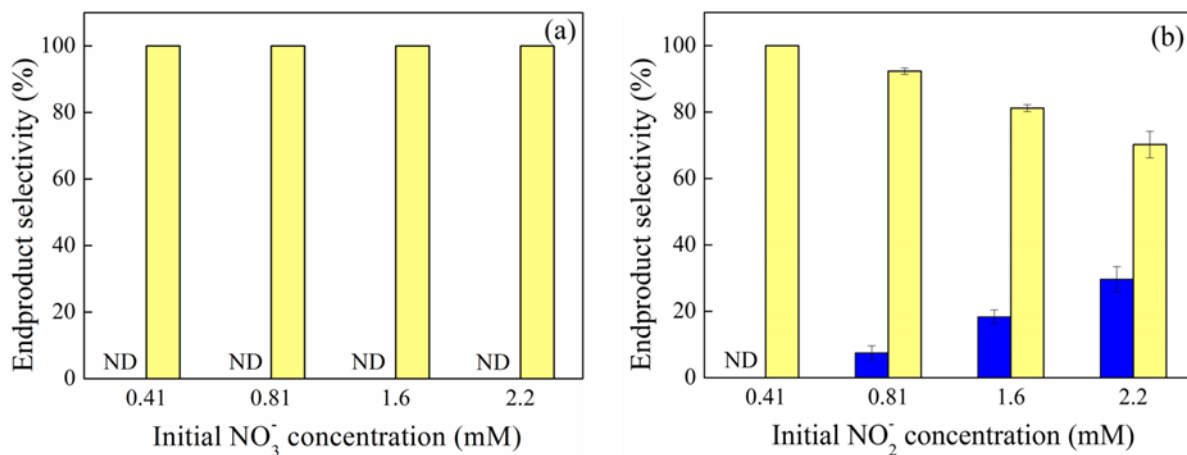
Figure 3.9 Effect of initial (a) nitrate and (b) nitrite concentration on NH_4^+/N_2 product selectivity (yellow: NH_4^+; blue: N_2). Product selectivity is based on percent molar N concentration. Error bars represent standard deviations of triplicate measurements (smaller than symbol if not visible).

catalysts, where nitrite is much more reactive than the parent nitrate ion.[39, 73] Nitrite reaction with Pd/C at the same conditions shown in Figure 3.8a yields a TOF_0 of 57.7 ± 9.2 min^{-1}.

The isotope labeling mass balance closure experiment conducted with nitrite as a starting reactant (Figure 3.4b) further reveals a distinct behavior of Ru-catalyzed nitrite reduction. In contrast to the experiment initiated with nitrate, nitrite reduction yields a mixture of N_2 and ammonium endproducts, and N_2O is observed as a reaction intermediate. Whereas the sole product of nitrate reduction detected is ammonium irrespective of initial nitrate concentration (Figure 3.9a), the distribution of N_2:ammonium observed in nitrite reduction experiments shifts increasingly towards N_2 with increasing initial nitrite concentration (Figure 3.9b).

3.4.4 Site-limited reduction kinetics

As mentioned earlier, measured nitrite concentrations drop below pseudo-first-order kinetic model predictions as the reaction progresses and nitrite concentration decreases (Figure 3.8a). To examine this further, TOF_0 of nitrate and nitrite reduction were determined at varying initial concentration of each oxyanion. Results of these measurements (Figure 3.8b) reveal

contrasting behavior for nitrate and nitrite. For nitrate, the observed trend is consistent with the classical Langmuir-Hinshelwood model for heterogeneous reactions, where TOF_0 increases with increasing initial nitrate concentration until it approaches a maximum value due to saturation of available surface reaction sites.[84] Similar behavior has been documented for many heterogeneous catalytic reactions, including nitrate, nitrite, and bromate reactions with Pd-based catalyst.[33, 85, 86] The small drop in TOF_0 observed at the highest initial nitrate concentration tested may result from competitive adsorption between nitrate and H_2 on the same reaction sites.[87] A contrasting and atypical behavior is observed for nitrite, where TOF_0 values are greatest at the lowest initial nitrite concentration and decrease to minimum value with increasing nitrite concentration. To rationalize this trend within the framework of a Langmuir-Hinshelwood model requires an assumption that nitrite competes directly with H_2 for the same reaction sites and the former has a much higher affinity for the sites than the latter, thereby inhibiting uptake and dissociation of the required H_2 reductant at higher nitrite concentrations. An important implication of this finding is that the relative reactivities observed for nitrate versus nitrite (e.g., Figure 3.8a) are heavily dependent upon the initial oxyanion concentrations used in the reactions. The heightened reactivity of nitrite at low nitrite concentrations can also potentially explain why the species is not observed as a reaction intermediate during Ru catalyst reactions initiated with nitrate; when nitrite is formed at low concentrations on the catalyst surface, its rapid turnover under these conditions prevents detection in the overlying aqueous solution. The competition between nitrite and H_2 adsorption may also contribute to the observed shift in endproduct selectivity towards ammonium at lower initial nitrite concentration (Figure 3.9b); conversion of nitrite to ammonium has a relatively higher stoichiometric requirement for H_2 than reduction to N_2, so an increase in H_2:nitrite ratio could favor the pathway for ammonium production by increasing surface

coverage of hydrogen and decreasing surface coverage of nitrogen species. The decreasing nitrite concentration is also expected to reduce the rate of N-N pairing reactions necessary to N_2O and N_2. Detailed pathways will be discussed in the following section.

Since separate reactions conducted with nitrate and nitrate suggest that the oxyanions both compete with H_2 for chemisorption at Ru active sites, competitive reactions between the two oxyanions were further examined by reaction initiated with mixtures of nitrate and nitrite. Figure 3.8c shows the reaction of an equimolar mixture of nitrate and nitrite at the same conditions as the individual oxyanion reactions shown in Figure 3.8a. Interestingly, despite the fact that nitrite reacts slower than nitrate when the two oxyanions are reacted with Ru/C separately, the presence of nitrite severely inhibits nitrate reduction. Nitrate reduction kinetics proceeds in two phases. A severely inhibited reduction phase is observed while nitrite is present, but the reaction accelerates once the nitrite is fully depleted. Variation of the ratio of initial nitrate and nitrite confirmed competition between the two oxyanions for available catalysts reaction sites, since the initial rate of nitrate reduction in the first phase increases with increasing nitrate/nitrite ratio, which is the same case for nitrite reduction measured in the presence of nitrate (Table B.3 in Appendix B).

3.4.5 Proposed reaction pathway

Ru catalysts behave differently from Pd-based catalysts in nitrate reduction product selectivity. For example, Ru catalysts favor complete selectivity for ammonium (Figure 3.4a), in contrast with a mixture of ammonium and N_2 endproducts reported for Pd-based bimetallic catalysts.[23, 31] Consistently high (and possibly complete) selectivity for ammonium was observed for Ru catalysts under various solution pH, whereas the ratio between ammonium and N_2 varies with shifting pH conditions for Pd-based bimetallic catalysts.[31, 41, 88] On the other hand, Ru

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catalysts and Pd-based catalysts share similarity in nitrite reduction product selectivity. For Ru/C, the distribution of N_2:ammonium shifts increasingly towards N_2 with increasing initial nitrite concentration (Figure 3.9b), similar to trends reported for Pd-based catalysts.[89] Figure 3.1 depicts the generally accepted mechanism of nitrate reduction on Pd-based catalysts. The experimental observations of nitrite reduction with Ru catalysts appear to be consistent with the reaction pathways proposed for Pd-based catalysts. Reactions initiated with nitrite yield transient intermediates and endproducts consistent with the two parallel pathways for NO reduction (Figure 3.4b). It may not be straightforward to apply the scheme to nitrate reduction with Ru catalysts considering the differences mentioned above and that reactions initiated with nitrate show no detectable nitrite intermediate (Figure 3.4a). However, the lack of observed nitrite intermediate is consistent with the elevated turnover rate of this species observed at low initial concentrations (Figure 3.8b) and selective reactivity of nitrite in the presence of nitrate (Figure 3.8c). Along this line, the complete selectivity for ammonium is possibly a result of high selectivity to ammonium at low nitrite concentration (Figure 3.9b).

It should be pointed out that Figure 3.1 only provides a macroscopic picture for the reaction. When considering the reaction from the microscopic viewpoint, the mechanism involves much more diverse intermediates that are adsorbed on the surface or in the aqueous phase. To obtain molecular insights into the mechanism of the reaction over Ru, DFT calculations were conducted to evaluate the thermodynamics of adsorption and transformation steps. Adsorption energies and conformations of major reactants, hypothesized intermediates and products are provided in Table B.4 in Appendix B. The elementary steps underlying the reaction pathways in Figure 3.1 are illustrated in Figure 3.10, and the energetics of each step are listed in Table B5 in Appendix B. The strong adsorption of NO_2^- (-1.3 eV) and NO (-2.0 eV) from water

to the Ru cluster surface may be contributing to the fact that desorbed aqueous species of the latter two were never observed during reactions initiated with nitrate. The further sequential reduction of NO$_{ads}$ to NH$_{3,ads}$ occurs through a series of exothermic reaction steps. Previous observations of the complete selectivity for ammonium in reactions initiated with nitrate (Figure 3.9a) and the shift in endproduct selectivity towards N$_2$ for nitrite reactions conducted with higher initial aqueous concentrations (Figure 3.9b) indicate that buildup of aqueous nitrite concentrations is a prerequisite for the reaction pathway leading to diatomic nitrogen species. We found that initiating N-N coupling by reaction of the NO$_{ads}$ intermediate with aqueous nitrite is exothermic, and subsequent reduction of the resulting intermediate to form both the detectable N$_2$O intermediate and stable N$_2$ endproduct are also favorable. Some have proposed that NO$_{ads}$
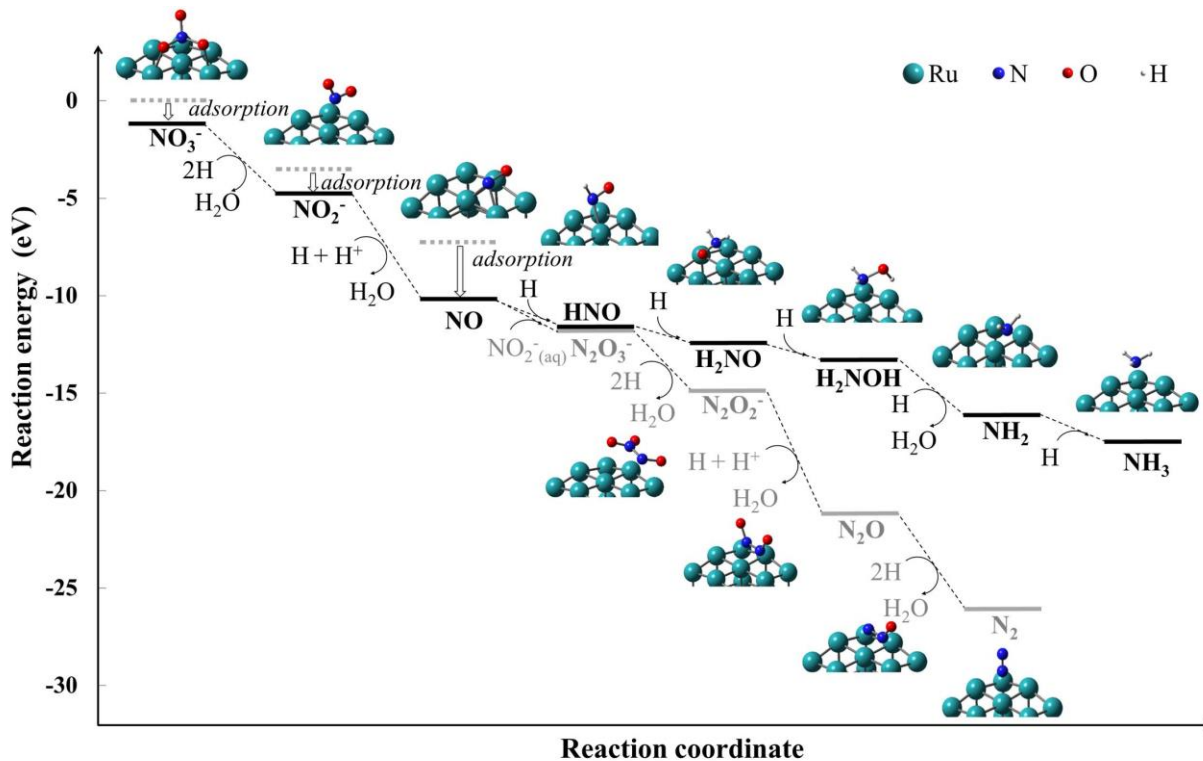
Figure 3.10 Energy profile of the most thermodynamically favorable reaction pathways for aqueous nitrate and nitrite reduction on Ru18 clusters as calculated using PBE0 functional and LANL2DZ (Ru)/6-31+G(d,p)(N, H, O) basis sets.

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dissociates first to N_{ads} and O_{ads} on catalyst metal surfaces before reacting further to form the observed products.[30, 89] DFT calculations indicate that this route cannot be ruled out based on energetics, but coupling between N_{ads} and NO_{ads} is unfavorable. The findings from DFT calculations that both reaction pathways are thermodynamically favorable implies that the kinetic factors, rather than thermodynamic constraints, are likely responsible for controlling the reaction product selectivity. Computing activation barriers and establishing microkinetic models will be needed to provide further insights into the reaction rates and endproduct selectivities observed in experiments.

3.4.6   Implications for technology development

The results of this study demonstrate that Ru catalysts effectively reduce nitrate at ambient temperature and H_2 pressure. Ru possesses many of the benefits of other Pt group metal catalysts (e.g., high stability) but is less expensive than Pd and Pt, showing potential to reduce barriers to catalyst technology adoption for treatment of recalcitrant water contaminants. The reductant (H_2) is low cost, can be generated on-site electrochemically, and has lower life-cycle environmental impacts than organic electron donors typically used in biological denitrification processes.[24] The catalysts used in the study are a commercially available material from a vendor capable to high volume production, making the process accessible to near-term commercial applications. The sole endproduct from nitrate reduction by the supported Ru catalysts investigated was ammonium, indicating that Ru catalysts are not suitable for treating drinking water with dilute nitrate in a single process. On the other hand, highly selective conversion of nitrate to ammonium, especially in concentrate matrices like waste ion exchange regenerant brines,[90] if followed by separation unit processes (e.g., membrane electrolysis[91]), may be a promising strategy for sustainably recovering an economically valuable product (e.g.,

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($(NH_4)_2SO_4$), which is in line with a growing interest in resource recovery from waste streams.[92] A number of technology development challenges remain to demonstrate viability, safety, and to de-risk the technology, but findings in this study suggest a path forward for development of an economical and sustainable technology for treatment and resource recovery from nitrate-contaminated water sources.

Rational design that emphasizes "design-for-purpose" is important to advance next-generation water treatment technologies.[93] Pt group metals are known to activate H_2. In order to couple H_2 oxidation with nitrate reduction, the activity of nitrate activation on Ru and the steps controlling selectivity need to be understood and is the objective of this study. Examination of the reaction mechanism revealed that selectivity for N_2 endproduct is limited during nitrate reduction with the Ru catalyst formulations examined here because N-N coupling requires significant aqueous nitrite concentrations to buildup and pairing between adsorbed N species is negligible. This suggests a target for future Ru catalyst design: tailor active sites for selective adsorption with nitrate over nitrite and/or reducing barriers to mobility and pairing of adsorbed N species. Surface alloying may be used to alter small molecule binding strength and rates of surface species diffusion.[94, 95] Alternatively, bio-inspired catalyst structures that attempt to mimic the multi-component features and activated metalloenzyme centers of biological systems may offer a promising strategy for enhancing catalyst activity. For example, Liu and co-workers recently demonstrated >100-fold improvement in catalytic reduction of the recalcitrant oxyanion perchlorate by modifying the Re component within Pd-Re/C bimetallic catalysts by complexing with oxazoline ligands that enhance the metal's oxygen atom transfer (OAT) reactivity,[96] mimicking the design of Mo-centered OAT metal complexes in the perchlorate reductase enzyme. Inspired by the heme-containing active sites of nitrate and (per)chlorate reductase, Ford

and co-workers constructed a non-heme iron complex for catalytic nitrate and perchlorate reduction, and the homogeneous catalyst is regenerated by electrons and protons provided by 1,2-diphenylhydrazine.[97] Biomimetic catalysts incorporating Ru as the active metal center for nitrate or nitrite reduction have not been reported to date.

3.5   Conclusions

Supported Ru nanoparticles showed promising catalytic performance in reducing nitrate in water at ambient temperature and H_2 pressure. It is demonstrated that Ru has a high intrinsic activity in nitrate activation, which is five times higher than that of Pd under standard testing conditions. The key features for supported Ru catalysts that need to be controlled to achieve high activity are that reduced Ru surface can be obtained by H_2 reduction at reaction temperature and that the surface is not blocked by synthesis residues. Ru reduces nitrate selectively to ammonium, while nitrite is reduced to yield a mixture of N_2 and ammonium, with selectivity shifting towards N_2 at increasing nitrite:hydrogen ratio. The reaction mechanism is proposed that sequential hydrogenation of nitrate to nitrite and NO is followed by parallel pathways involving the adsorbed NO: (1) sequential hydrogenation to ammonium, and (2) N-N coupling with aqueous nitrite followed by hydrogenation to the detected N_2O intermediate and N_2 endproduct. Future work is needed to strategically design catalyst to control selectivity and develop integrated processes for nitrogen recovery.

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CHAPTER 4

RUTHENIUM CATALYSTS FOR REDUCTION OF *N*-NITROSAMINE WATER
CONTAMINANTS

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4.1 Abstract

N-nitrosamines have raised extensive concern due to their high toxicity and detection in

treated wastewater and drinking water. Catalytic reduction is a promising alternative technology

to treat *N*-nitrosamines, but to advance this technology pathway, there is a need to develop more

efficient and cost-effective catalysts. We have previously discovered that commercial catalysts

containing ruthenium (Ru) are unexpectedly active in reducing nitrate. This study evaluated

supported Ru activity for catalyzing reduction of *N*-nitrosamines. Experiments with *N*-

nitrosodimethylamine (NDMA) show that contaminant is rapidly reduced on both commercial

and in-house prepared Ru/Al_2O_3 catalysts, with the commercial material yielding an initial metal

weight-normalized pseudo-first-order rate constant (k_0) of 1103 ± 133 L g_{Ru}^{-1} h^{-1} and an initial

turnover frequency (TOF_0) of 58.0 ± 7.0 h^{-1}. NDMA is reduced to dimethylamine (DMA) and

ammonia end-products, and a small amount of 1,1-dimethylhydrazine (UDMH) was detected as

a transient intermediate. Experiment with a mixture of five *N*-nitrosamines spiked into tap water

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(1 µg L^{-1} each) demonstrates that Ru catalysts are very effective in reducing a range of *N*-nitrosamine structures at environmentally relevant concentrations. Cost competitiveness and high catalytic activities with a range of contaminants provide strong argument for developing Ru catalysts as part of the water purification and remediation toolbox.

4.2   Introduction

N-nitrosamines are a class of compounds with a nitroso group bonded to a secondary amine (R$_1$R$_2$N-NO). These compounds are of great health concern due to their elevated carcinogenicity and genotoxicity.[1] Much of the current focus on *N*-nitrosamines, especially *N*-nitrosodimethylamine (NDMA), is related to their occurrence in water sources and formation as disinfection byproducts (DBPs) during drinking water and wastewater treatment.[2] NDMA contamination events that have received considerable spotlights include the detection of up to 40 µg L^{-1} NDMA in municipal wells and surface water in Ontario, Canada,[3] and the detection of high levels (up to 400 µg L^{-1}) in groundwater at a rocket engine testing facility in California, USA.[4] The World Health Organization (WHO) has established a guideline value of 0.1 µg L^{-1} for NDMA in drinking water.[5] Although there is currently no federal maximum contaminant level (MCL) for *N*-nitrosamines in drinking water, the U.S. EPA included NDMA and four other *N*-nitrosamines on the fourth Contaminant Candidate List (CCL4).[6] The awareness of *N*-nitrosamine formation as a byproduct from drinking water disinfection processes and the advancement in analytical methods have resulted in widespread detection of NDMA in sourcewater and treated water samples.[7] The growing interest in potable reuse of municipal wastewater, particularly in water-limited regions, further increases concerns about exposure to *N*-nitrosamines because of their chemical recalcitrance and ability to pass through the final reverse osmosis membranes barrier typically used in such facilities.[4, 8]

It follows that there has been extensive research conducted on NDMA treatment technologies. Currently, UV photolysis is the major treatment technology applied specifically to treat NDMA,[4, 9] producing dimethylamine (DMA) and methylamine (MA) as terminal endproducts.[10] While effective, the high UV fluences required an order-of-magnitude higher than fluences typically applied for disinfection purposes,[4, 11] leading to high costs and energy use. Powdered activated carbon,[12] nanofiltration, and reverse osmosis,[13] have been reported to effectively remove NDMA precursors. However, these physical removal processes are ineffective for N-nitrosamines themselves, especially for lower molecular weight N-nitrosamines like NDMA.[13, 14] Chemical destruction can be achieved by advanced oxidation process such as ozone/hydrogen peroxide,[15] but these processes are inefficient due to the non-selective nature of the hydroxyl radical oxidants and the presence of elevated concentrations of non-target radical scavengers in most water sources (e.g., HCO_3^- and natural organic matter).

The reducibility of N-NO group has inspired research on reductive processes as an alternative treatment strategy for N-nitrosamines. Mezyk and co-workers reported a bimolecular rate constant for the reaction of hydrated electron (e_{aq}^-, E_H = -2.9 V)[16] with NDMA (1.41×10^{10} M^{-1} s^{-1}) that is two orders-of-magnitude higher than that reported for reaction with hydroxyl radical (4.30×10^8 M^{-1} s^{-1}).[17] Practical generation of hydrated electrons requires application of UV light together with elevated concentrations of a photo-sensitizer, often KI or K_2SO_3, and alkaline pH conditions (e.g., pH > 9).[18] Corrosion of zerovalent metals, such as iron, in water can generate adsorbed atomic hydrogen atom, but the slow kinetics reported for these processes[19] and buildup of a hazardous intermediate[20] prompted a search for more efficient catalysts for generating adsorbed atomic hydrogen. To date, the majority of studies have focused on Pd-based catalysts[21-24] due to their high activity and stability in aquatic matrices. However, the high and

variable cost of Pd[25] has limited the further development and adoption of reductive catalytic water treatment technologies. Initial evaluation of alternative low-cost Ni-based catalysts (e.g., Raney Ni) reported high activities for *N*-nitrosamine reduction,[26] but further development was limited by safety concerns associated with the pyrophoric properties of porous Ni catalysts, poor catalyst stability in aqueous matrices, and health concerns related to leaching of Ni into product water. Thus, there continues to be strong interest in the development of alternative catalysts for *N*-nitrosamine reduction that are effective, stable, and less costly than Pd-based materials.

As part of a larger effort aimed at expanding the range of metals that can be applied for reductive treatment processes, we recently found supported Ru materials to be very active for catalyzing aqueous nitrate and nitrite reduction with H_2 under room temperature and atmospheric pressure.[27] No intermediate was detected during nitrate reduction, suggesting that proposed intermediates such as nitrite and nitrous oxide at low concentrations are rapidly converted. This represents a potential breakthrough because the cost of Ru is historically much lower than Pd. The high activity of Ru observed with nitrate and its NO_x intermediates is suggestive of potential for catalyzing reduction of the N-NO group within *N*-nitrosamine structures. The overall goal of this contribution is to test this hypothesis and to examine reactivities of NDMA and related *N*-nitrosamine contaminants with supported Ru catalysts under relevant water quality conditions. Reaction kinetics and products for NDMA with Ru catalysts are examined and compared to Pd-based catalysts, and reaction of mixture of *N*-nitrosamine structures spiked at trace levels (1 μg L^{-1} each) into tap water is evaluated to validate the applicability of the technology to relevant treatment conditions. Finally, the activity of Ru and Pd catalysts with a suite of aquatic contaminants is compared to assess the broad applicability of Ru-based catalysts as substitutes for Pd catalysts.

4.3 Experimental Section

4.3.1 Chemicals

Neat *N*-nitrosodiethylamine (NDEA), *N*-nitrosopiperidine (NPIP), and *N*-nitrosomorpholine (NMOR) were purchased from Ultra Scientific. Neat NDMA and *N*-nitrosodi-n-propylamine (NDPA), dimethylamine (DMA) solution (40 wt% in water), 1-fluoro-2,4-dinitrobenzene, 4-nitrobenzaldehyde, 4-chlorophenol, 4-nitrophenol, sodium diatrizoate hydrate, triethylamine, NH_4Cl, MES hydrate pH buffer, H_3PO_4 (85 wt% in water), and NaH_2PO_4 were obtained from Sigma-Aldrich. Isotopically labeled standards [6-^{2}H] NDMA (NDMA-d_6, 98%) and [14-^{2}H] NDPA (NDPA-d_{14}, 98%) (1000 mg L^{-1} in dichloromethane) were acquired from Cambridge isotope laboratories. 1,1-dimethylhydrazine (unsymmetrical dimethylhydrazine, UDMH) hydrochloride was purchased from TCI America. Methanol, acetonitrile, dichloromethane, acetic acid, Na_2SO_4, NaOH, and HCl were obtained from Fisher. Ultra-high purity H_2, Ar, and N_2 were supplied by General Air.

4.3.2 Catalyst preparation and characterization

The majority of experiments used a commercial Ru/Al_2O_3 (nominal 5 wt% Ru) catalyst from Sigma-Aldrich. A separate Ru/Al_2O_3 material was also prepared from $Ru(NO)(NO_3)_3$ (Alfa Aesar) aqueous solution and Al_2O_3 (Sigma-Aldrich) using an incipient wetness impregnation technique.[28] Commercial Pd/Al_2O_3 (nominal 5 wt% Pd) was also obtained from Sigma-Aldrich and used to prepare a bimetallic $Pd-In/Al_2O_3$ catalyst with $In(NO_3)_3 \cdot 3H_2O$ (Alfa Aesar) aqueous solution following a reported method.[22] Prior to use, dry catalysts were *ex situ* reduced in flowing H_2 at 120 °C for 1 h before cooling to room temperature in flowing Ar.

Actual metal contents of the catalysts were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (PerkinElmer 5300DV) after digestion in HF-HCl-

HNO$_3$ (for Pd catalysts) or by alkaline fusion (for Ru catalysts). Surface area and pore structure analyses were determined by N$_2$ BET adsorption-desorption isotherms measured at 77 K using a Micromeritics ASAP 2020 analyzer. Dispersion of Ru or Pd was determined by CO chemisorption using an assumed 1:1 CO:Metal adsorption stoichiometry.[29, 30] For Pd-In/Al$_2$O$_3$ catalysts, CO was assumed to be chemisorbed only on Pd surfaces. Morphology of the Ru nanoparticles was characterized by high angle annular dark field (HAADF) imaging with scanning transmission electron microscopy (FEI Titan S/TEM operated at 200 kV). To obtain the particle size distribution, at least 150 particles were counted for each image.

4.3.3 Catalytic reduction of NDMA

Catalyst activity was evaluated in a semi-batch system under continuous H$_2$ sparging (1 atm, 200 mL min^{-1}) at room temperature (22 ± 0.5 °C). The relatively high H$_2$ flow rate was used to ensure solution saturation of H$_{2(aq)}$ and minimize potential H$_2$ gas-to-aqueous mass transfer limitations during experiments. A 250 mL round-bottom flask was filled with desired mass of catalyst and 120 mL 10 mM 4-morpholineethanesulfonic acid (MES) pH buffer at pH 6.0. The catalyst suspension was mixed by magnetic stirring and sparged with H$_2$ for 3 h before introducing a small volume of concentrated aqueous NDMA stock solution to initiate the reaction. The effect of stirring speed on reaction rate was evaluated in preliminary tests, and a stirring speed of 900 rpm was chosen to eliminate external mass transfer limitations. Aliquots were then collected at predetermined times to monitor the disappearance of NDMA. H$_{2(aq)}$-free control tests were conducted by sparging catalyst suspension with H$_2$ for 3 h followed by Ar for 1 h before adding the NDMA stock solution. In one set of experiments, the reduction of repeated spikes of NDMA was monitored in the semi-batch reactor to evaluate catalyst stability and potential deactivation. The volume of NDMA stock solution used for each spike was carefully

calculated to achieve an initial concentration of 100 µM in the resulting solution. Mass-normalized rate constants were calculated for each spike. The overall repeated-spike test was run in duplicate.

Catalyst activity was assessed by quantifying initial metal weight-normalized pseudo-first-order rate constants (k_0, L $g_{Ru/Pd}^{-1}$ h^{-1}) and turnover frequencies (TOF$_0$, h^{-1}), defined as the number of NDMA molecules reduced per surface Ru/Pd atom per hour. Initial observed pseudo-first-order rate constants ($k_{obs,0}$, h^{-1}) were determined by fitting the natural log of substrate concentration versus time data for the first reaction half-life, and the corresponding mass-normalized rate constants were determined by:

$$k_0 = \frac{k_{obs,0}}{C_{catalyst} W_{metal}}$$ (4.1)

where $C_{catalyst}$ is the catalyst mass loading in the aqueous suspension (g L^{-1}), and W_{metal} is the metal wt fraction of the catalyst. The corresponding TOF$_0$ value was then calculated by dividing the initial NDMA reduction rate (R_0, mol L^{-1} h^{-1}) by the concentration of surface Ru or Pd atoms ($C_{metal\ surface}$, mol L^{-1}):

$$TOF_0 = \frac{R_0}{C_{metal\ surface}} = \frac{k_{obs,0} C_0}{(Dispersion \times C_{catalyst} W_{metal})/M}$$ (4.2)

where R_0 is the product of $k_{obs,0}$ and the initial NDMA concentration (C_0, mol L^{-1}), and $C_{metal\ surface}$ is estimated from dispersion coupled with information on $C_{catalyst,}$ W_{metal} and the atomic weight of Ru or Pd (M, g mol^{-1}). Experiments with other reducible substrates, e.g., 4-nitrophenol, 4-chlorophenol, and diatrizoate, followed the same protocol as that for NDMA.

Endproduct distributions and carbon/nitrogen balances were quantified using closed-system batch experiments. The reactor setup was the same as that described above, except that the reactor was sealed immediately after introducing NDMA stock solution (to prevent

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volatilization of selected products during continuous H_2 sparging). Aliquots were collected at predetermined times for analysis of NDMA plus its daughter products.

4.3.4   Catalytic reduction of *N*-nitrosamines under environmentally relevant conditions

An experiment was conducted to validate that the reactions observed with NDMA described apply to a range of *N*-nitrosamines and to conditions relevant to water treatment operations (i.e., natural water matrix with trace initial concentrations of *N*-nitrosamines). Tap water was initially heated to approximately 80 °C to volatilize free chlorine. Composition of the tap water, including alkalinity, total dissolved solids (TDS), common anions and metals, total organic carbon (TOC), ammonium and pH are provided in Table C.1 in Appendix C. Several replicate reactors were then prepared by adding 400 mL of the tap water and 40 mg of catalyst to a 500 mL amber graduated media bottle equipped with an Omnifit T Series Bottle Cap and Teflon-coated stir bar, and the catalyst suspension was mixed and sparged with H_2 for 3 h before introducing an aqueous stock mixture of NDMA, NDEA, NDPA, NPIP, and NMOR (1 µg L^{-1} of each *N*-nitrosamine) to initiate the reaction. The procedure was repeated several times, with the entire contents of the bottle being sacrificed for extraction and analysis of *N*-nitrosamines after different reaction times. The bottle contents were vacuum filtered through a 0.45 µm mixed cellulose esters membrane to remove catalyst particles before solid phase extraction. The same protocol was followed in a separate experiment using deionized water for comparison. To test *N*-nitrosamine adsorption to the catalyst, the same amount of catalyst, tap water, and aqueous *N*-nitrosamine mixture stock solution was mixed in the absence of H_2 sparging.

A control test for *N*-nitrosamine adsorption to the catalyst was conducted by mixing the same amount of catalyst, tap water, and aqueous *N*-nitrosamine mixture stock solution in the absence of H_2 sparging.

4.3.5 Analytical methods

NDMA, 4-chlorophenol, 4-nitrophenol, and diatrizoate were directly analyzed by HPLC with UV/vis photodiode array detector (Shimazu SPD-M20A) and a Waters Spherisorb ODS2 Column (4.6 mm × 150 m, 5 µm packing material). DMA and UDMH were analyzed by the same equipment after pre-column derivatization. Composition and flow rate of mobile phase, detection wavelength, and derivatization protocols followed published methods.[19, 26, 31-34] Ammonia was quantified using the Hach salicylate method (low range, 0.02 to 2.50 mg L^{-1} NH$_3$-N, method 10023). Dissolved Ru was measured by ICP-AES (PerkinElmer 5300DV).

For tests with *N*-nitrosamine mixture at environmentally relevant concentrations, water samples were fortified with the surrogate NDMA-d_6 at the final concentration of 0.5 µg L^{-1} and extracted by passing filtered reaction solution through a solid phase extraction (SPE) cartridge filled with 2 g of coconut charcoal (Restek). The cartridge was conditioned with dichloromethane, methanol, and Nanopure water according to EPA Method 521.[35] The extract was passed through a drying column packed with 6 g of anhydrous sodium sulfate and concentrated by N$_2$ blow down. After addition of internal standard NDPA-d_{14} at the final concentration of 100 µg L^{-1}, the volume was adjusted to 2 mL with dichloromethane, and the sample was analyzed by a TSQ 8000 Evo Triple Quadrupole GC-MS/MS (ThermoFisher) with electron impact ionization. A Rxi-5Sil MS column (30 m × 0.32 mm I.D. × 0.25 µm film thickness) was operated under the following oven temperature program: initial temperature 35 °C was held for 4 min, raised first to 60 °C at 5 °C min^{-1} and then to 80 °C at 4 °C min^{-1}. The injector was heated at 250 °C, and the injection volume was 1 µL in the splitless mode. Transfer line and ion source temperatures were held at 250 °C and 220 °C, respectively. A calibration

curve covering the range 10-300 µg L^{-1} was corrected for the surrogate recovery. Each sample was analyzed in triplicate.

4.4   Results and Discussion

4.4.1   Catalytic NDMA reduction activity

Control experiments confirmed that aqueous NDMA cannot be reduced by H$_2$ in the absence of catalysts, and loss of NDMA by adsorption to the catalyst support is insignificant (Figure C.1 in Appendix C). Commercial Ru/Al$_2$O$_3$ shows significantly higher activities than either Pd/Al$_2$O$_3$ or Pd-In/Al$_2$O$_3$ catalysts under the same conditions (Figure 4.1). The estimated Weisz-Prater parameter (C$_{WP}$) was found to be <<1 (see Section C.1 in Appendix C), indicating that the internal mass transfer within the catalyst support particles is not rate limiting. This is an interesting finding given that Pd-based materials are considered the state-of-the-art catalysts for NDMA and related contaminants.

The initial reaction rate increases with initial NDMA concentration and plateaus at higher NDMA concentrations (Figure C.2a in Appendix C), which has been observed for NDMA reduction on Pd-based[36] and Ni catalysts,[26] and is described by the Langmuir- Hinshelwood model[37] for surface-mediated reactions. Assuming that NDMA and hydrogen adsorb non-competitively to Ru surface sites and that the surface reaction is rate-limiting, the Langmuir-Hinshelwood model can be expressed as

$$r_0 = k_{rxn} \frac{K_{ads}[NDMA]_0}{1 + K_{ads}[NDMA]_0} \qquad (4.3)$$

where r$_0$ is the metal weight-normalized initial NDMA reduction rate (mol g$_{Ru}$$^{-1}$ h^{-1}), k$_{rxn}$ is the rate constant (mol g$_{Ru}$$^{-1}$ h^{-1}) for adsorbed NDMA reacting with adsorbed atomic hydrogen, K$_{ads}$ is
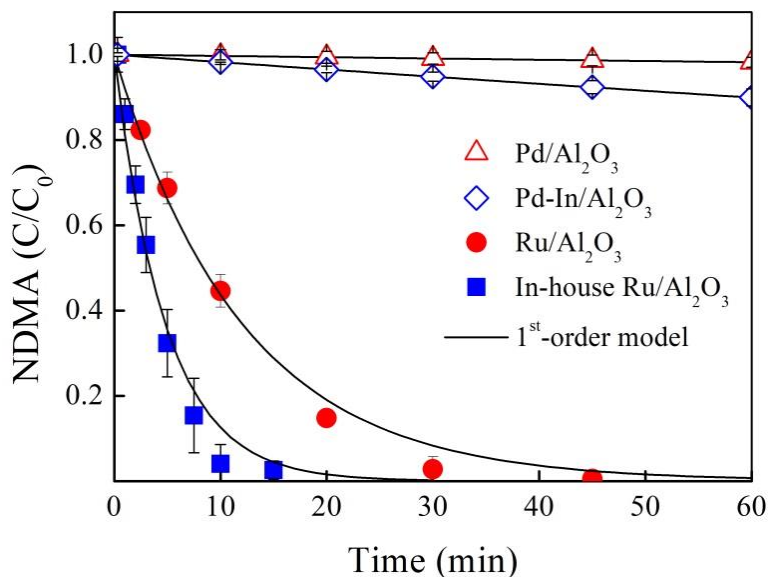
Figure 4.1 Timecourse of NDMA reduction with different catalysts in the semi-batch reactor system ([NDMA]$_0$ = 100 μM, 0.1 g L^{-1} catalyst, pH 6.0 buffered by 10 mM MES buffer, continuous sparging of 1 atm H$_2$, 22 ± 0.5 °C). Error bars represent standard deviations of triplicate reactions. Catalyst formulation details provided in Table 4.1.

the equilibrium adsorption constant (mol^{-1} L) for NDMA on the catalyst surface, and [NDMA]$_0$ is the initial aqueous concentration (mol L^{-1}). A plot of reaction rate versus NDMA concentration according to Eq. 4.3 features a linear region at low NDMA concentrations where reaction rate increases proportionally with initial NDMA concentration. At higher initial NDMA concentrations, further increases in reaction rate are less than proportional and eventually plateau as surface reaction sites become saturated. This trend is consistent with the Langmuir-Hinshelwood kinetic model for surface reaction processes (Eq. 4.3). It is observed from Figure S2 that the initial NDMA concentration used in most experiments (100 μM) was not within the linear region of the Langmuir-Hinshelwood model. To estimate the pseudo-first-order rate constant in the linear region, which is constant and characteristic of reaction kinetics at more environmentally relevant concentrations of NDMA (e.g., < 1 μg L^{-1}), Eq. 4.3 was fit to experimental data by nonlinear least squares regression, and two model parameters, k_{rxn} and K_{ads}, were determined to be 0.15 ± 0.01 mol g$_{Ru}^{-1}$ h^{-1} and 33,500 ± 5,900 mol^{-1} L (uncertainty

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represents 95% confidence limits), respectively. Therefore, the metal weight-normalized pseudo-first-order rate constant in the linear region was calculated to be 5,030 L g_{Ru}^{-1} h^{-1}. Compared with other catalysts reported to date (Table C.2 in Appendix C), the commercial Ru/Al$_2$O$_3$ shows extremely high activity for catalyzing NDMA reduction (e.g., Pd/Al$_2$O$_3$ and Pd-In/Al$_2$O$_3$ catalysts all reported < 100 L g_{Pd}^{-1} h^{-1}). Density functional theory (DFT) study of NDMA decomposition over Ni and Pd surfaces showed that NDMA has stronger binding on the Ni surface than on Pd.[38] It follows that the high activity of Ru catalysts is potentially related to stronger binding of NDMA on Ru surface. However, further computational studies of NDMA and intermediate adsorption energies and the activation energies of rate-determining steps on metal surfaces are needed to evaluate this rationale.

A second Ru/Al$_2$O$_3$ was synthesized in lab and compared with the commercial Ru/Al$_2$O$_3$. Physical properties of catalysts are summarized in Table 4.1. At comparable catalyst mass loadings, the in-house prepared Ru/Al$_2$O$_3$ shows 150% increase in NDMA reduction activity compared with the commercial Ru/Al$_2$O$_3$ (Figure 4.1, Table C.2 in Appendix C). The greater activity is attributed to higher Ru dispersion or smaller Ru nanoparticle size. Commercial Ru/Al$_2$O$_3$ has a wide distribution of Ru particle sizes with an average value of 4.5 nm (Figure 4.2a). In comparison, in-house prepared Ru/Al$_2$O$_3$ has more evenly distributed fine nanoparticles, with average particle size of 1.9 nm (Figure 4.2b). Note that the average particle size and distribution may vary slightly when increasing the number of particles counted. However, when reaction rates are normalized to Ru surface sites, the estimated TOF$_0$ of NDMA on in-house prepared Ru/Al$_2$O$_3$ is lower than that estimated for commercial Ru/Al$_2$O$_3$ (Table 4.1), indicating that the reaction is sensitive to the surface structure of the supported Ru nanoparticles.[39] Comparing the TOF$_0$ values to Pd catalysts shows that the intrinsic reactivity of Ru surfaces with

NDMA is approximately two orders-of-magnitude higher than that of Pd surface and In-promoted Pd surfaces (Table 4.1). Previously, the most active catalyst reported was a 2.4%Pd0.6%Ni/γ-Al$_2$O$_3$ catalyst that exhibited a TOF of 1.0 h^{-1} at an initial NDMA concentration of 2 μM.[36] Due to the dependence of TOF$_0$ on initial NDMA concentration, it is not rigorous to directly compare values in Table 4.1 with reports from the literature. To overcome this challenge, TOF$_0$ on commercial Ru/Al$_2$O$_3$ at an initial NDMA concentration of 2 μM was estimated by combining Eqs. 4.2 and 4.3, where all the variables are known. The resulting TOF$_0$ was estimated to be ~6.0 h^{-1}, six times greater than that reported for the optimized Pd-Ni/γ-Al$_2$O$_3$ catalyst.

Table 4.1 Properties of catalysts used for NDMA reduction activity test.

Catalyst	BET surface area (m^2 g^{-1})	Total pore volume[a] (cm^3 g^{-1})	Average pore diameter[b] (nm)	Metal loading (wt%)[c]	Metal dispersion (%)	Particle size (nm)	TOF$_0$ (h^{-1})
Commercial Ru/Al$_2$O$_3$	86.3	0.23	10.8	4.51	19	4.5 ± 2.8	58.0 ± 7.0
In-house Ru/Al$_2$O$_3$	122.0	0.21	7.0	4.58	81	1.9 ± 0.7	34.1 ± 4.0
Commercial Pd/Al$_2$O$_3$	94.7	0.22	9.4	4.59	31	ND[d]	0.14 ± 0.05
Pd-In/Al$_2$O$_3$	94.4	0.22	9.3	4.43 (Pd) 0.87 (In)	45[e]	ND	0.56 ± 0.12

[a]Adsorption total pore volume at P/P$_0$ = 0.98. [b]Calculated from total pore volume and BET surface area. [c]Measured by ICP-AES analysis. [d]Not determined. [e]CO was assumed to be chemisorbed only on Pd surface.

The stability of Ru/Al$_2$O$_3$ for NDMA reduction was evaluated by repeatedly spiking NDMA into a semi-batch reactor and comparing rates of NDMA disappearance over repeated reaction cycles. Activities of the Ru/Al$_2$O$_3$ showed slight variation over 7 consecutive reaction cycles (Figure C.3 in Appendix C). Analysis of dissolved Ru in the reaction solution collected at the end of the last reaction cycle was below the detection limit of the ICP-AES method ($\leq$ 0.14 μg L^{-1}). Ultimately, on-stream continuous treatment studies are needed to assess catalyst stability,
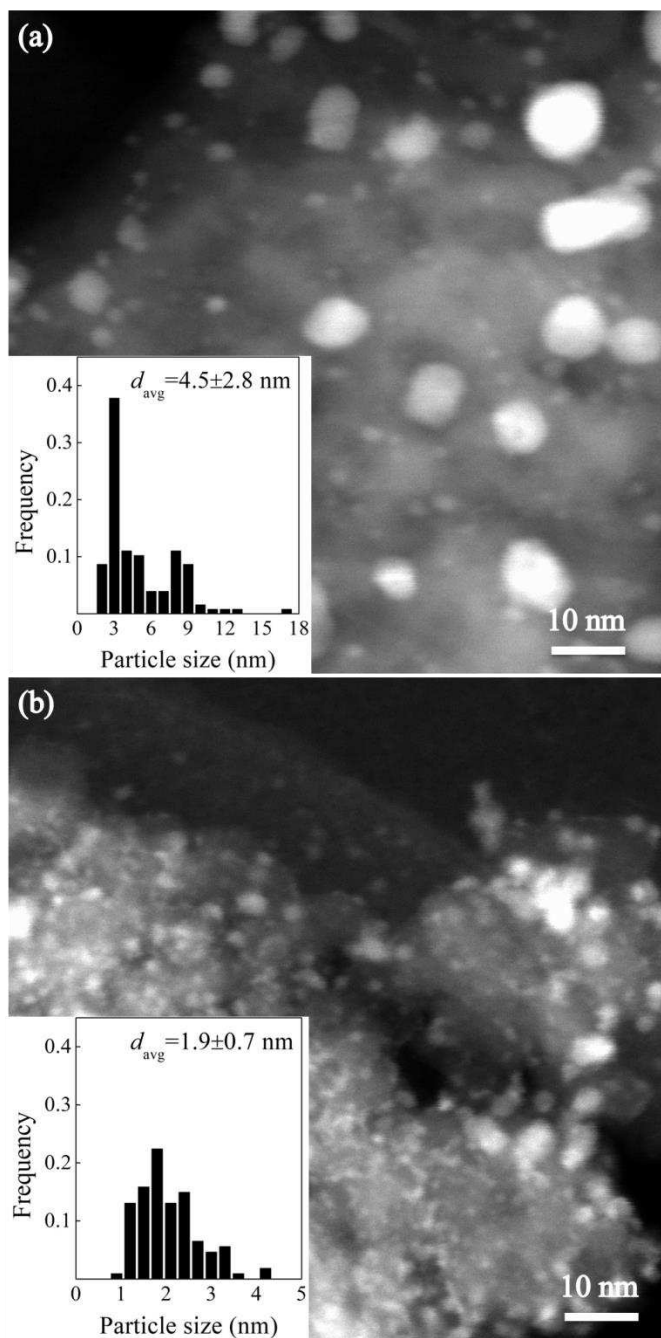
Figure 4.2 HAADF-STEM images of (a) commercial Ru/Al_2O_3 and (b) in-house prepared Ru/Al_2O_3. The insets show Ru particle size distributions.

but results from these initial tests are suggestive of a stable catalytic process with minimal

potential for Ru leaching. It is also worth noting that for this study we chose to use Al_2O_3-

supported Ru catalysts to avoid potential artifacts from N-nitrosamine adsorption to

carbonaceous supports and facilitate comparison with other Al_2O_3-supported catalysts reported in the literature (Table C.21 in Appendix C), but previous work examining nitrate reduction found greater activity for carbon-supported Ru catalysts than Al_2O_3-supported Ru catalysts.[27] Future research is suggested to examine the influence of catalyst supports in order to optimize practical treatment applications.

4.4.2 NDMA reduction products

Figure 4.3 shows the disappearance of NDMA and formation of intermediates and endproducts on Ru/Al_2O_3. A carbon mass balance (Figure 4.3a) was mostly closed by using NDMA and endproduct DMA, but a small amount (<2%) of UDMH was also detected as a transient intermediate during the reaction. The largest deviation in the carbon mass balance (<4%) occurred at an early stage of the reaction, and is likely a result of summing species measured using different methods. The nitrogen mass balance (Figure 4.3b) also showed stoichiometric generation of ammonia in addition to DMA. Although reactor headspace was not analyzed, the good nitrogen mass balance strongly suggests a high, and possibly complete, selectivity to ammonia. The high selectivity to ammonia was consistent across a wide range of solution pH conditions (Figure C.4 in Appendix C). Therefore, reduction of NDMA yielded quantitative amounts of DMA and ammonia according to the following stoichiometry, consistent with oxidation of 3 equivalents of H_2.

$$\text{N}\text{—}\text{N}\text{=}\text{O} + 3H_2 + H^+ \longrightarrow \text{NH} + NH_4^+ + H_2O \qquad (4.4)$$
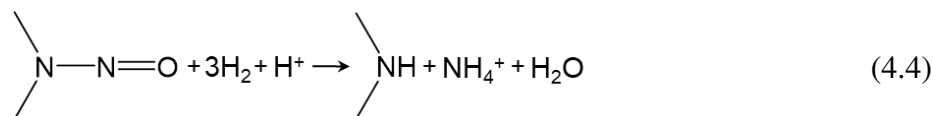
The quantitative formation of DMA as an endproduct is widely reported in reductive transformation of NDMA, such as with granular iron and Fe enhanced iron,[19] Ni,[21, 26] Pd and bimetallic Pd catalysts.[21, 36] Recent studies on zerovalent Fe and Zn observed a loss of nitrogen

mass during reduction of NDMA and UDMH, and attributed this to ammonia and other unmeasured products.[7, 20] Considering the high metal dose (10 g L^{-1}) employed in these earlier studies, the loss of nitrogen may result of adsorption to metal surfaces, as observed with granular iron.[19] Organic amines (either DMA or MA) are a product of most reported treatment processes for NDMA,[10, 15, 19, 22] so their complete elimination and complete mineralization of NDMA remains a general challenge if that is ultimate treatment objective. In comparison, the fate of nitrosyl group in NDMA during reduction depends on catalyst (Table C.2 In Appendix C).
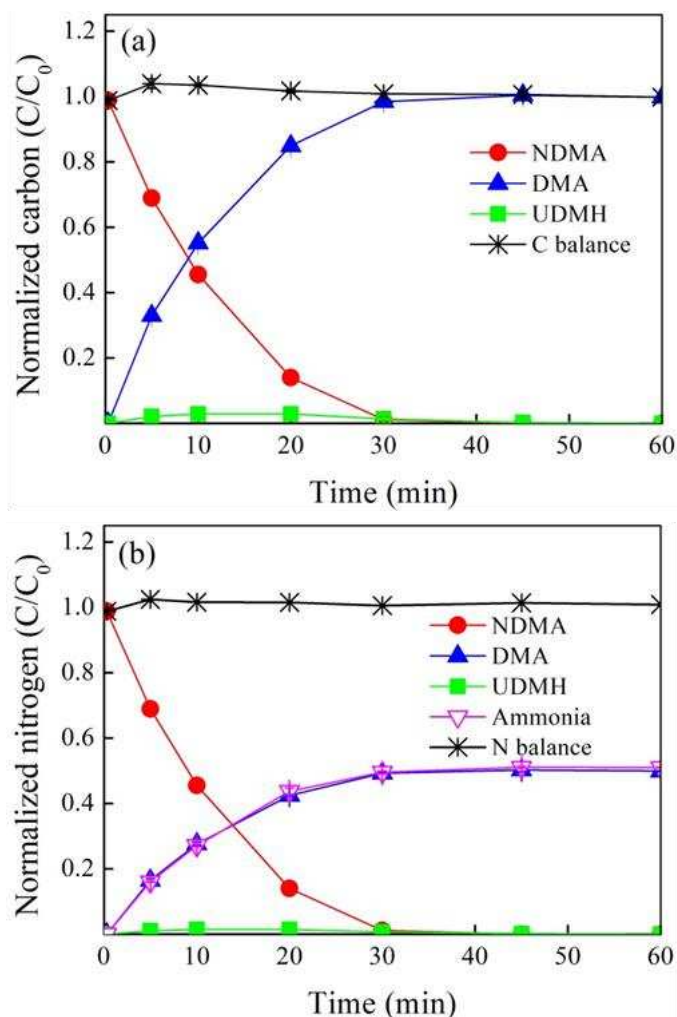
Figure 4.3 (a) Carbon and (b) nitrogen balance of NDMA reduction on commercial Ru/Al$_2$O$_3$ in the batch system ([NDMA]$_0$ = 100 μM, 0.1 g L^{-1} catalyst, pH 6.0 buffered by 10 mM MES buffer, 1 atm H$_2$, 22 ± 0.5 °C). Error bars represent range of results from duplicate reactions (smaller than symbol if not visible).

Similar to granular Fe[19] and Pd-based catalysts,[22] Ru reduces the nitrosyl group ultimately to ammonia. In contrast, this group was found to be reduced to N_2 by porous Ni catalysts.[26] Modification of Ni catalyst with boron changes product selectivity from N_2 to ammonia.[40] It is also worth noting that the endproducts, DMA and ammonia, are both much less hazardous than NDMA.[19] Furthermore, the concentrations of these endproducts that would form from typically detected concentrations of NDMA (≤ 1 µg L^{-1}) are much lower than typical concentrations of ammonia and DMA in natural water matrices.[41, 42] Still, if necessary, these products can be oxidized chemically or biologically by introduction of a separate unit process.

4.4.3 Mechanistic considerations

As a member of Pt-group metals, Ru has low activation energy for dissociative adsorption of H_2 on its surface at ambient temperature.[43, 44] Thus, like Pd-based catalysts, Ru-catalyzed reduction of NDMA is expected to proceed by NDMA reaction with Ru-adsorbed atomic hydrogen. A question with less obvious answer is whether there also exists a direct electron transfer reaction between reduced Ru surface atoms and NDMA. Thermodynamic considerations indicate that redox reaction is not likely. Previous study of NDMA reduction with granular iron concluded that adsorbed atomic hydrogen resulting from iron corrosion in water was responsible for NDMA reduction rather than direct electron transfer from Fe(0). This was concluded because the measured reduction potential of the Fe grains ($\geq$ -0.52 V) are higher than the required potential for reducing NDMA (approximately -1.3 V at NDMA concentrations of a few millimolar and more negative at NDMA concentrations below 1 mM).[45] Ru(0) is an even weaker reducing agent than Fe(0). For example, the formal standard reduction potential of $Ru^{2+}/Ru(0)$ is +0.455 V, much higher than that of $Fe^{2+}/Fe(0)$ (-0.447 V).[46] Mediated electron transfer through the redox couple Ru^{3+}/Ru^{2+} (+0.2487 V) is also not close to the value required

for NDMA reduction. Figure C.1 in Appendix C confirms that without addition of H_2, no NDMA reduction occurs in Ru catalyst suspensions (catalyst suspension was pre-sparged with H_2 to ensure reduction of Ru surface atoms, but then sparged with Ar to remove dissolved H_2 from the suspension before adding NDMA). Thus, NDMA reduction most likely proceeds via hydrogenation by surface-adsorbed atomic hydrogen.

Postulated pathways of aqueous NDMA reduction with various metals mainly differ in the sequence of cleaving two bonds, i.e., N=O bond and N-N bond. Initial hydrogenation/cleavage of N=O bond features the formation of UDMH, which was only experimentally observed in systems where metal acts as sacrificing electron donor, including aluminum-nickel alloy in alkaline solution,[47, 48] Zn powder,[20, 49] and Cu(II) promoted Fe powder.[7] Therefore, it is an interesting observation that small quantities of UDMH are detected from NDMA reduction on Ru surface with H_2 as an electron donor (Figure 4.3a). Experiments initiated with UDMH show slower overall reduction kinetics than observed for NDMA reduction across a range of initial substrate concentrations (Figure C.5a in Appendix C), justifying the observed UDMH generation during NDMA reduction.

Based on experimental observations in this study and insights from previous studies, a hypothesized NDMA reduction mechanism on Ru is presented in Figure 4.4. According to the Langmuir-Hinshelwood reaction mechanism, NDMA and H_2 adsorb onto Ru surface and get activated. The N=O bond of NDMA is initially hydrogenated and subsequently cleaved to form UDMH. Subsequently, scission of N-N bond in adsorbed UDMH results in unstable surface-bound DMA and amine fragments that are rapidly reduced by surface hydrogen atoms to produce the observed DMA and ammonia endproducts, consistent with the selective production of ammonia from UDMH reduction (Figure C.5b in Appendix C).
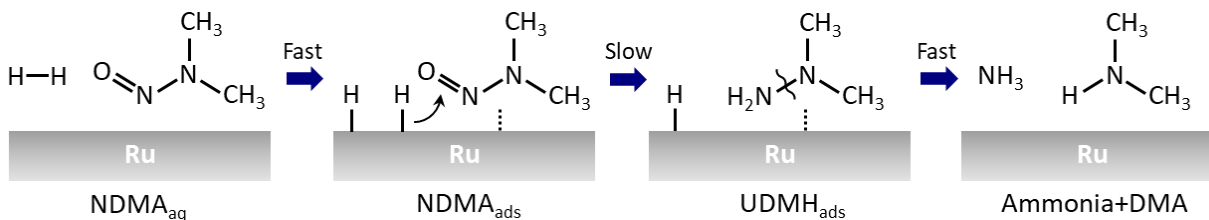
Figure 4.4 Proposed mechanism of NDMA reduction on Ru catalyst surfaces.

4.4.4   Catalytic reduction of *N*-nitrosamines under environmentally relevant conditions

Although high concentrations of NDMA (tens to hundreds of parts per billion) have been detected in groundwater at a rocket engine testing facility in Sacramento County, CA,[4] more often the concentrations concerning wastewater and drinking water treatment facilities are ≤ 1 ug L^{-1}.[9] There is very limited study assessing catalytic technologies for NDMA or other *N*-nitrosamines at these environmentally relevant concentrations. To further demonstrate the applicability of Ru catalysts, five *N*-nitrosamines (1 μg L^{-1} each) were simultaneously reduced with Ru/Al$_2$O$_3$ in tap water. Control experiments show little loss of *N*-nitrosamines due to adsorption in the absence of H$_2$ (data not shown). When H$_2$ sparging is present, concentrations of all five *N*-nitrosamines rapidly decreased (Figure 4.5). Data from two replicates were fitted with a pseudo-first order rate law by nonlinear least squares, and the optimal rate constants were obtained with uncertainty representing 95% confidence limits. All five *N*-nitrosamines tested are reduced at rates on the same order of magnitude, similar to the observation of four dialkyl *N*-nitrosamines and one diphenyl *N*-nitrosamine reduction catalyzed by porous nickel catalyst.[26] The metal weight-normalized pseudo-first-order rate constant for NDMA, NDEA, NDPA, NMOR, and NPIP are 5,700 $\pm$ 490, 3,530 $\pm$ 430, 2,950 $\pm$ 510, 10,400 $\pm$ 300, 7,510 $\pm$ 690 L g_{Ru}^{-1} h^{-1}, respectively. The observed rate constant for NDMA is comparable to that derived from extrapolation of the Langmuir-Hinshelwood model down to the initial concentration of 1 ug L^{-1}
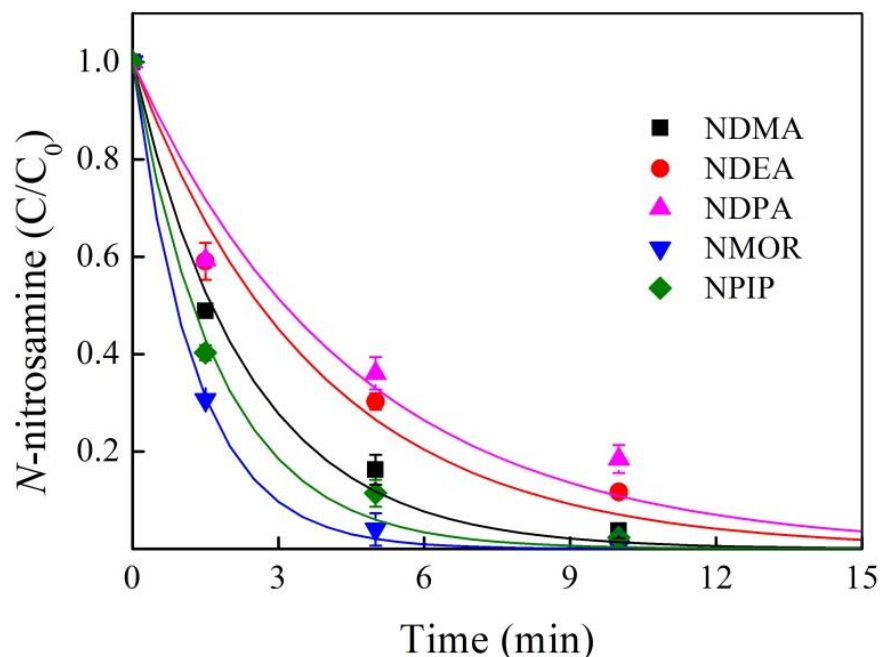
Figure 4.5 Catalytic reduction of a mixture of N-nitrosamines added to tap water (1 ug L^{-1} of each N-nitrosamine, 0.1 g L^{-1} commercial Ru/Al$_2$O$_3$ catalyst, initial solution pH 9.0, continuous sparging of 1 atm H$_2$, 22 ± 0.5 °C). Lines show pseudo-first-order model fits for disappearance of each N-nitrosamine. Error bars represent the range of measured values in duplicate reactions (smaller than symbol if not visible).

(5,030 L g$_{Ru}^{-1}$ h^{-1}). While differences in the observed rates for the five N-nitrosamines were small, comparison of fit-derived rate constants reveals a relationship between molecular structure (Figure C.6 in Appendix C) and reactivity. For dialkyl N-nitrosamines, increasing length of alkyl group reduces reactivity, and N-heterocycle N-nitrosamines show higher reactivity than dialkyl N-nitrosamines. The reduction of N-nitrosamines observed in deionized water at these same N-nitrosamine concentrations is faster than in tap water (Figure C.7 in Appendix C), indicating that water matrix constituents in the tap water negatively affect catalyst activity. Future research is needed to examine in detail water matrix effects on Ru catalyzed water treatment processes, which will complement findings reported for Pd-based catalysts and advance the practical development of catalytic processes for treating contaminated sourcewaters of varying

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composition. Nonetheless, the findings presented here verify effective catalytic treatment of *N*-nitrosamines at realistic micropollutant concentrations in a relevant water matrix.

4.4.5 Role of Ru catalysts in water purification and remediation toolbox

Traditional strategies to reductively transform water contaminants employ materials containing zerovalent Fe.[50, 51] Despite their competitiveness in price, the inefficiency for removing certain contaminants,[21, 52] stringent requirement of solution pH,[53] sacrificial nature and generation of iron oxides waste[36] prompted research for more effective and sustainable materials. Hydrogenation metal-based materials have emerged as a promising alternative. Particularly, Pd-based catalysts have demonstrated their superior performance and stability in reducing a number of drinking water contaminants.[24, 54, 55] The fact that Pd exhibits poor activity for reduction of selected contaminants, together with the scarcity and the high cost of this metal, necessitates an expansion of the catalyst toolbox and improved mechanistic understanding of metal-catalyzed hydrogenation reactions. We have explored other Pt group metals in addition to Pd for catalytic reduction of oxyanions, and gained new understanding of reaction mechanisms of oxyanions with different metals.[25] Motivated by promising results for nitrate reduction with Ru, a contribution focusing on a renewed evaluation of the kinetics and mechanisms of nitrate and nitrite reduction by supported Ru catalysts followed.[27] The strong adsorption of nitrite and postulated reduction intermediate, nitrous oxide, and the rapid conversion of these species at low concentrations prompted the hypothesis that Ru is potentially effective for catalyzing the reduction of other water contaminants containing nitro and nitroso functional groups. This contribution reveals the extremely high activity of Ru for catalyzing the reduction of *N*-nitrosamines, including the ubiquitous contaminant NDMA, supporting the abovementioned hypothesis. To further explore the strength of Ru catalysts in water purification and remediation,

we screened Ru/Al_2O_3 and Pd/Al_2O_3 catalysts for reduction of a suit of contaminants featuring different reducible functional groups (Figure C.8 in Appendix C). Contrary to expectations, Ru is nearly one order-of-magnitude less active than Pd for 4-nitrophenol reduction. Without further in-depth investigation, an initial examination of the molecule structure suggests that the phenol group in 4-nitrophenol can affect activity in at least two ways. The presence of benzene ring and the hydroxyl group alter the adsorption geometry of nitro group, and the benzene ring donates electron to the nitro group, modifying its electron density and subsequently the adsorption energy. Despite the influence of phenol group, the TOF_0 measured for 4-nitrophenol on Ru is similar to those measured for nitrate and NDMA. We also tested Ru/Al_2O_3 activity with halogenated arenes (4-chlorophenol and diatrizoate). The activities are in the same order of magnitude as nitrate, NDMA and 4-nitrophenol. In comparison, Pd/Al_2O_3 showed much higher activity for substituted arene reduction than nitrate and NDMA reduction. Activities of Pd/Al_2O_3 for reducing 4-nitrophenol, 4-chlorophenol and diatrizoate are 6.1, 3.3, and 1.1 times higher than those of Ru/Al_2O_3, respectively. Considering the price of Ru is roughly one order-of-magnitude lower than that of Pd,[25] Ru can still be a viable alternative to Pd for treating these contaminants. It is also worth mentioning that Ru is also an exceptional catalyst for oxidation of water contaminants with permanganate,[56, 57] ozone,[58] and peroxymonosulfate,[59] making it a versatile heterogeneous catalyst for water purification and remediation. Still, further research is needed to assess Ru catalyst activity and stability during continuous treatment (e.g., in packed bed reactors) of relevant water matrices. Such studies will be critical to demonstrating the feasibility this and related technology pathways.

4.5   References

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CHAPTER 5

A HYBRID CATALYTIC HYDROGENATION/MEMBRANE DISTILLATION PROCESS
FOR NITROGEN RESOURCE RECOVERY FROM NITRATE-CONTAMINATED WASTE
ION EXCHANGE BRINES

This chapter is in preparation

Xiangchen Huo, Johan Vanneste, Tzahi Y. Cath, and Timothy J. Strathmann

5.1   Abstract

Ion exchange is a common approach to treating nitrate-contaminated ground water. To reduce salt usage and waste brine disposal following from resin regeneration, catalyst treatment systems have been evaluated and show promise for reducing both life cycle costs and environmental impacts. Past efforts focused on improving nitrate removal kinetics and selectivity to the N_2 reduction product versus NH_3, but the potential value of nitrogen resources has been overlooked in this approach. This work evaluated a hybrid catalytic hydrogenation/membrane distillation process for nitrogen resource recovery from nitrate-contaminated waste ion exchange brines. A commercial Ru/C catalyst with high selectivity for ammonia production was tested for nitrate hydrogenation and showed capability to reduce a wide concentration range of nitrate under typical waste brine conditions, including conditions representative of expected salt buildup upon brine reuse. The apparent rate constant for nitrate reduction was influenced by both solution chemistry and reaction temperature. In the second stage of the hybrid process, membrane distillation efficiently recovered ammonia from the brine matrix, capturing nitrogen

X.H. performed most of the experiments and analyzed data; J.V. and Z.Y.C. assisted membrane distillation experiments and provided helpful advice; X.H. and T.J.S. wrote the manuscript with input from all authors. All authors are affiliated with Colorado School of Mines.

as ammonium sulfate, a commercial fertilizer product. At low temperatures (<35 °C), solution pH significantly influenced the ammonia mass transfer coefficient through the membrane by controlling the fraction of free ammonia species present. Ammonia recovery efficiency was not affected by salt levels, indicating the feasibility of membrane distillation for recovering ammonia from reused brine as well. Application of the hybrid catalytic hydrogenation/membrane distillation process to a real ion exchange waste brine showed both high rates of nitrate hydrogenation and ammonia recovery. These findings provide alternative lower-cost catalyst for treatment of ion exchange waste brine to allow for both waste brine reuse and nitrogen resource recovery.

5.2   Introduction

Industrial nitrogen fixation through energy-intensive Haber-Bosch process has been playing a critical role in sustainable food supply. However, a significant portion of this nitrogen resource exits agricultural and industrial activities as waste and enters surface and ground waters, endangering aquatic environments and ecosystems.[1] Particularly, nitrate in drinking water has been recognized as a human health hazard, for which health guidelines and regulations have been established to protect populations from its adverse effects. Therefore, there has been a considerable interest in developing technologies for nitrate removal from impacted drinking water sources.[2-5]

Ion exchange is a common approach to treating nitrate-contaminated ground water and has been proven effective at multiple drinking water treatment plants.[6] Due to their finite exchange capacities, anion exchange resins (AER) require periodic regeneration using a concentrated salt solution (commonly sodium chloride or sodium bicarbonate). This regeneration process results in nitrate-contaminated waste brine, incurring operation and maintenance (O&M)

costs associated with brine makeup and disposal.[7, 8] Disposal of waste brine containing regenerant salt residue also reduces salt use efficiency and increases fresh salt demand, which significantly increases O&M costs.[9] Thus, strategies to increase salt use efficiency and minimize brine waste are critical to improving the economics and environmental sustainability on ion exchange processes for drinking water treatment.

Transforming nitrate to gaseous species or aqueous species that have much lower affinity to the AER can potentially enable brine recycling and minimize salt inputs. The highly oxidized state of nitrogen in nitrate allows it to be reductively transformed, either biologically, chemically or catalytically.[10-14] Efforts have typically focused on selectively converting nitrate to gaseous N_2 and minimizing byproduct formation including nitrite, $N_2O_{(g)}$, and ammonia.[2, 15, 16]

Catalytic hydrogenation is among the emerging nitrate transformation technologies and considered to have potential for industrial applications.[17, 18] Advantages of this technology include short start-up times, fast reactions, use of a clean reducing agent that can be produced renewably (H_2), low possibility of bacterial contamination, and minimal production of contaminated disposals.[5, 19-22] The most common reactor configurations for catalytic hydrogenation are three-phase reactors (e.g., semi-batch, fixed bed) where a metal surface catalyzes aqueous nitrate reduction by $H_{2(g)}$, a reductant with lower life cycle environmental impacts than organic donors used for biological reduction.[23] Supported bimetallic Pd catalysts (e.g., Pd-Cu, Pd-In, Pd-Sn) have been most extensively studied due to their high activity and tunable selectivity towards N_2.[16, 19, 24-26] Studies with these catalysts have shown that some natural water constituents can significantly influence catalyst reactions with nitrate through competitive adsorption or modification of catalyst surface.[27-29] These results are particularly important as they predict inhibitory effects of high salt levels ion exchange waste brines, which

were confirmed for Pd-In catalysts in recent studies performed in brine matrices.[8, 21, 22] Despite these reports, brine reuse enabled by catalytic hydrogenation of nitrate is a promising strategy to significantly bring down salt costs and reduce environmental impacts associated with conventional ion exchange treatment processes.[21, 22]

Reductive transformation of concentrated nitrate in ion exchange brine, including catalytic hydrogenation, often results in ammonia formation.[15, 22, 30] Although selectivity to ammonia has typically been deemed undesirable when directly treating drinking water, ammonia species have potential value as fertilizer products. Therefore, conversion to ammonia can be advantageous if a suitable process for recovering the endproduct is available, and opportunities for recovering ammonia are most practical in matrices where nitrate concentrations are elevated like waste brines (where nitrogen concentrations can reach g/L levels).[15, 31, 32] In this work, we describe efforts aimed at evaluating a hybrid catalytic hydrogenation/membrane distillation process for ion exchange waste brine nitrate treatment and nitrogen recovery (Figure 5.1). Specifically, we assessed treatment of nitrate-contaminated ion exchange waste brines using a commercial Ru/C catalyst, an alternative to much more costly Pd-based catalysts, which was recently reported to exhibit complete selectivity to ammonia when treating nitrate-contaminated freshwater matrices.[4] The catalytic hydrogenation process was studied in a stirred semi-batch reactor, a reactor design suitable for treating highly concentrated nitrate solutions.[21] Membrane distillation was then applied to recover the ammonia product from the waste brine as ammonium sulfate $(NH_4)_2SO_4$, a potentially valuable fertilizer product.[33-35] Experiments using synthetic waste solutions were conducted to identify critical operating parameters of both the hydrogenation and membrane distillation processes, and a demonstration of the integrated process with real ion exchange waste brine obtained from a drinking water utility is presented.

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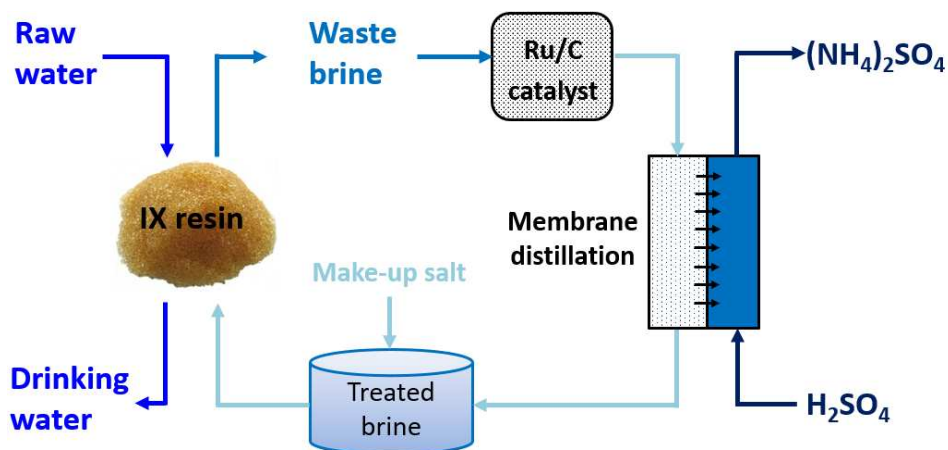
Figure 5.1 Flow diagram of the hybrid catalytic hydrogenation/membrane distillation process to enable ion exchange regenerant brine reuse and nitrogen resource recovery.

5.3   Materials and Methods

5.3.1   Materials

Ru/C catalyst powder with a nominal Ru loading of 5 wt% was purchased from Sigma Aldrich and used as received. Detailed characterization of this material was described previously.[4] This catalyst exhibited high surface area and Ru metal dispersion. Sodium nitrate and ammonium chloride were also obtained from Sigma Aldrich. Sodium sulfate, sodium bicarbonate, ammonium hydroxide solution, sodium hydroxide, and hydrochloric acid were acquired from Fisher Scientific. Concentrated sulfuric acid was purchased from EMD Millipore. Ultra-high purity H_2 gas was supplied by General Air. Ion exchange waste brine was collected from a drinking water treatment plant in California. Composition of the waste brine is summarized in Table 5.1.

5.3.2   Catalytic hydrogenation experiments

To determine the influence of operating parameters on nitrate hydrogenation efficiency, kinetic studies were conducted with synthetic brine solutions using a procedure adapted from a previous study.[4] Predetermined mass of Ru/C and a test solution (120 mL) of designed salt

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concentrations (NaCl, NaHCO$_3$, and/or Na$_2$SO$_4$) were added to a 250 mL three-neck flask equipped with rubber stoppers and a Teflon-coated magnetic stir bar. The loading of Ru/C was chosen to achieve a condition where external mass transfer limitations are absent. Prior to the reaction, Ru/C was reduced overnight in the suspension (constant stirring, 1100 rpm) at room temperature under 1 atm H$_2$ headspace by flowing H$_2$ gas through the reactor (300 mL min^{-1}). Reaction was initiated by adding a concentrated NaNO$_3$ stock solution (5 M) to achieve the designed initial nitrate concentration (50-200 mM). Reaction temperature was maintained with a water bath calibrated by an external thermometer. The change of solution pH over the course of reaction was monitored by using a pH probe (Orion™ double junction combination pH electrode, calibrated by standard NIST buffers, apparent pH values were reported). In the case where the effect of pH on reactions was evaluated, solution pH was maintained by adding HCl solution from an automatic pH-stat (Metrohm). Aliquots of the catalyst suspension (1.5 mL) were periodically collected by a syringe and immediately filtered (0.45 µm cellulose acetate) to quench the reaction. The filtrate was diluted with deionized water and analyzed for nitrate, nitrite, and/or ammonia concentrations. All experiments were performed in duplicate.

The procedure for catalytic hydrogenation of real waste brine was modified to avoid the complication of parallel *in situ* catalyst reduction and nitrate reduction. Prior to the reaction, a Ru/C slurry (0.6 g Ru/C in 10 mL deionized water) was reduced overnight under H$_2$ flow (300 mL min^{-1}) at room temperature. Reaction was then initiated by introducing 100 mL waste brine to the flask containing the pre-reduced catalyst. As a control, experiments were also conducted in a synthetic brine prepared to mimic the major ion composition of the real waste brine. For tests with CO$_{2(g)}$ as a pH buffer, CO$_2$ was introduced to the reactor at 65 mL min^{-1}. The rest of the procedure follows that as previously described. A catalyst recycle experiment was also carried

Table 5.1 Ion exchange waste brine composition.

Component	Concentration (mg/L)
pH	8.5
Inorganic C	3,057
DOC	8.8
Alkalinity	13,100 mg/L as $CaCO_3$ (232 mM as $NaHCO_3$)
Major anions	
Cl^-	13,685 (2.3 wt% as NaCl)
NO_2^-	<15 (detection limit)
NO_3^-	9,262 (149 mM)
SO_4^{2-}	4,346 (45 mM)
PO_4^{3-}	<15 (detection limit)
Major cation	
Na^+	16,860
Other metals	
K	35.7
Mg	15.8
Ca	5.8
Cr	2.9
V	1.2
Li	0.6
Mo	0.5
Sr	0.2

out to evaluate the reusability of Ru/C for waste brine treatment. At the end of the reaction, the catalyst was collected by filtering the suspension with a membrane filter (0.45 µm cellulose acetate), washed with deionized water several times, and dried in air at 70 °C before reusing.

5.3.3 Membrane distillation experiments

A bench-scale membrane distillation assembly was operated in batch mode to recover ammonia from synthetic solutions or catalytically hydrogenated real waste brine (Figure 5.2). The membrane cell was custom-made acrylic plastic cell, and spacers were used in both the feed and the acid adsorbent channels of the cell. A hydrophobic, microporous membrane acquired from Clarcor Industrial Air (QL822) was tested in this study. The membrane is a polypropylene backed PTFE membrane having a nominal pore size of 0.45 µm with the functional layer in contact with the feed. Three cells were used in sequence, and each cell had a membrane surface area of 195 cm^2. The experiments were performed using co-current flow to minimize the local

pressure differential across the membrane. The feed stream was pumped continuously during operation using a positive-displacement gear pump (Micropump Integral Series, IDEX Corp. Vancouver, WA). The acid adsorbent stream was pumped continuously using a peristaltic pump (Masterflex L/S Series, Cole-Parmer, USA). Flow rates of the feed and the acid adsorbent were kept equal. A heat exchanger was used to control the temperature of the feed stream. Membrane integrity was tested prior to experiments to validate integrity and ensure that the membranes are not wetted.

Four liters of feed solution was used for each batch experiment. Sulfuric acid solution (0.25 M, 1-2 L) was prepared from concentrated sulfuric acid and used as acid adsorbent. Kinetic studies were conducted with synthetic solutions to examine the impact of operating parameters on ammonia recovery efficiency. The synthetic solutions were prepared by dissolving predetermined amount of salts (NaCl, NaHCO$_3$, and/or Na$_2$SO$_4$), NH$_4$OH aqueous solution, and base (NaOH) in deionized water. The amount of NH$_4$OH and NaOH was determined through the following reaction stoichiometry assuming complete hydrogenation of nitrate:

$$NO_3^- + 4\,H_2 \;\rightarrow\; NH_4OH + OH^- + H_2O \qquad\qquad (5.1)$$
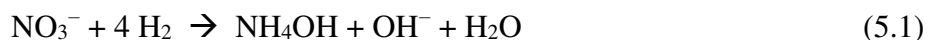
Time zero was recorded once the feed reached the designed temperature (heat-up time 1-2 min), and the test duration was 60 min. The initial pH of the feed and pH at the end of a test were recorded. Feed solution was sampled periodically (8-10 mL) to track the change of total ammonia concentration. For selected tests, acid adsorbent solution was also sampled (1 mL) to evaluate the mass balance on ammonia in the system. Batch experiments were performed in duplicate. The procedure for catalytically treated real waste brine was the same as for synthetic solutions.
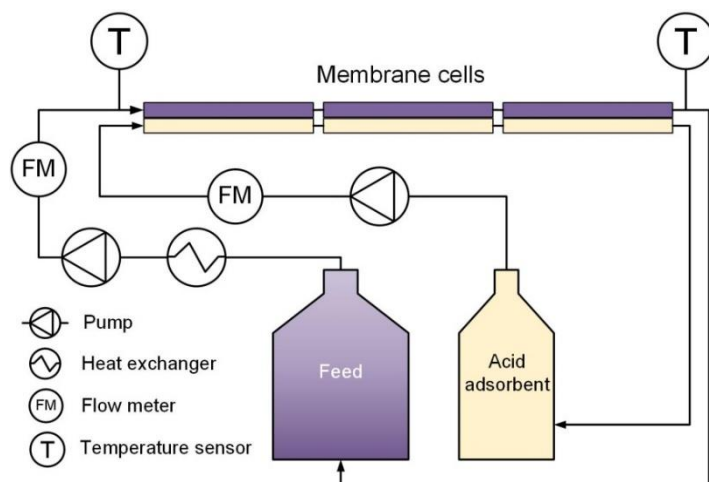
Figure 5.2 Schematic diagram of the bench scale membrane distillation system.

5.3.4 Aqueous analysis

Anions, including Cl^-, NO_3^-, SO_4^{2-}, NO_2^-, and PO_4^{3-}, were quantified by ion chromatography with conductivity detection (ICS-90, Dionex, Sunnyvale, CA). Metals were quantified by inductively coupled plasma–atomic emission spectroscopy (ICP-AES; Optima 5300, Perkin-Elmer, Fremont, CA). ICP samples were acidified with nitric acid to a pH <2 before analysis. Total ammonia (NH_3/NH_4^+) was analyzed by colorimetric analysis (Hach salicylate method). Alkalinity was measured by titration with 1 N H_2SO_4. Dissolved organic carbon (DOC) and inorganic carbon were determined using a total organic carbon analyzer (Shimadzu TOC-L, Columbia, MD).

5.4 Results and Discussion

5.4.1 Catalytic hydrogenation of nitrate

Catalytic hydrogenation tests with Ru/C were initially conducted in synthetic brine solutions to assess the influence of major anions and operating conditions on nitrate hydrogenation rates. A baseline testing condition was chosen to facilitate the evaluation process, where an initial $NaNO_3$ concentration of 100 mM was reduced in a brine matrix (5 wt% NaCl,

100 mM NaHCO$_3$, 100 mM Na$_2$SO$_4$) at 30°C without controlling solution pH. The elevated initial concentration was selected to mimic conditions observed previously in waste ion exchange regenerant brines.[15, 22] To verify that reaction rates were not subject to external mass transfer limitations, the initial nitrate hydrogenation rate was measured for catalyst loadings ranging from 1 to 7.5 g L^{-1}. It was observed that the initial reaction rate linearly increased with the catalyst loading (Figure D.1 in Appendix D), consistent with no external mass transfer limitation. However, the possibility of internal mass transfer limitation cannot be ruled out. A catalyst loading of 5 g L^{-1} was then selected to use in subsequent experiments.

The kinetics of nitrate hydrogenation with Ru/C under baseline testing condition can be characterized by the zero-order rate law to at least the first half-life (Figure 5.3). Similarly, zero-order kinetics has been observed for hydrogenation of concentrated nitrate (81 mM) with Pd-In/C catalyst in both freshwater and synthetic brine solutions, and was attributed to saturation of active catalyst surface sites by the elevated concentrations of nitrate and other anions.[21] To obtain a quantitative description of apparent catalyst activity for comparison with other operating conditions and literature values, the experimental data were fit with a zero-order kinetic model (Eq. 5.2) to the first half-life:

$$C_{nitrate,\ t} = C_{nitrate,\ 0} - k_0 t \qquad (5.2)$$

where $C_{nitrate,\ 0}$ is the initial nitrate concentration (mM), $C_{nitrate,\ t}$ is the nitrate concentration at reaction time t (min), k_0 is the apparent zero-order rate constant (mM min^{-1}). To compare catalyst activity with existing literature, k_0 was normalized to Ru mass (mM min^{-1} g$_{Ru}^{-1}$) by using loading of Ru metal in the reactor suspension (g$_{Ru}$ L^{-1}). Under the baseline testing condition, k_0 was found to be 0.30 ± 0.03 mM min^{-1} g$_{Ru}^{-1}$. This value falls within the same order-of-magnitude as values reported for Pd-In/C catalysts using a similar semi-batch reactor (11-50 mgNO$_3^-$ min^{-1} g$_{Pd}^-$

^{1}),^{21} suggesting that applying Ru/C for nitrate hydrogenation in ion exchange waste brine is technically feasible. This is also notable because Ru is significantly less expensive than Pd.[4, 36 59]

The influence of critical operating parameters, including solution pH, salt levels, initial nitrate concentration, and temperature, were then evaluated. Because the reaction produces hydroxide (or consumes proton) as shown in Eq. 5.1, the solution pH increases as nitrate hydrogenation proceeds in the absence of a buffer. Under the baseline condition, solution pH increased from an initial value of 9.5 to 12.6 by the end of the reaction (Figure 5.3). To evaluate the potential influence of solution pH, apparent zero-order rate constants were determined for reactions where pH was maintained by automatic pH-stat (with HCl addition). Two solution pH conditions were tested, circum-neutral (pH 7.5) and basic (pH 11). The difference in catalyst activity between these two conditions was within 20% (entries no. 2 and 3 in Table 5.2), with the apparent rate constant slightly higher under basic conditions. At first glance, the limited effect of solution pH appears to conflict with findings reported previously for the same catalyst reacting with lower initial nitrate concentrations (1.6 mM), where the first-order reaction constant decreased at high pH conditions.[4] The inhibitory effects of increasing hydroxide ion concentrations has been reported for hydrogenation of nitrite and bromate with Pd catalysts and attributed to the inhibition of oxyanion adsorption as surfaces become more negatively charged at high pH conditions.[37-39] However, the hydroxide concentrations under the two solution pH conditions (0.32 µM for pH 7.5 and 1.0 mM for pH 11) are considerably lower than nitrate concentration in the brine matrix, explaining the much smaller difference between the apparent zero-order rate constants observed here. In the absence of pH control (entry no. 4 in Table 5.2), the apparent zero-order rate constant increased 46%, despite the rapid increase in solution pH. This observation suggests that the chloride introduced during pH control (from use of HCl in the
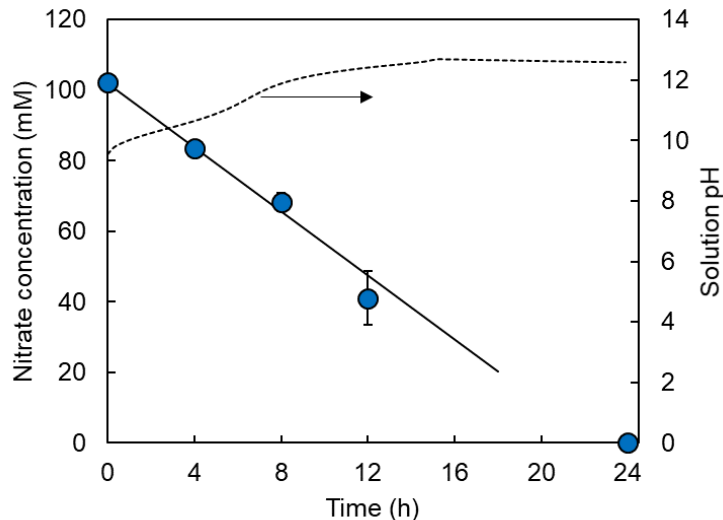
Figure 5.3 Catalytic nitrate hydrogenation under baseline testing condition and evolution of solution pH. Conditions: 5 g L^{-1} Ru/C, initial $[NO_3^-]$ = 100 mM, brine matrix (5 wt% NaCl, 100 mM $NaHCO_3$, 100 mM Na_2SO_4), 30°C, no solution pH control, 1 atm H_2 headspace maintained by flowing H_2 at ca. 300 mL min^{-1}. Error bars indicate standard deviation from duplicate measurements (smaller than symbol if not visible). Solid line indicates zero-order rate law fit. Dashed line indicates change in measured pH during the reaction.

pH stat) may have inhibitory effects on nitrate hydrogenation activity.

Three major non-target anions in waste brines and reused brines (i.e., chloride, bicarbonate, and sulfate) were then examined for their influence on nitrate hydrogenation activity. These anions have been reported to exert negligible or negative effects on nitrate reduction with Pd-based catalysts.[21, 22, 29] Therefore, it was surprising to find that the apparent rate constant observed in the absence of all these anions was 40% lower than that observed under the baseline condition. Unlike chloride and sulfate, bicarbonate is acid-base reactive. Tests were then performed to evaluate bicarbonate and the two other anions separately. With a solution containing only bicarbonate and nitrate (entry no. 5 in Table 5.2), the observed rate constant increased significantly to 0.58 ± 0.01 mM min^{-1} g_{Ru}^{-1}, more than twice the rate observed under the baseline condition, suggesting an inhibitive effect of chloride and sulfate anions. This conclusion was confirmed by results at higher salt levels (entry no. 6 in Table 5.2), where a two-

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Table 5.2 Summary of nitrate hydrogenation szero-order rate constants under different reaction conditions (1 atm H_2, Ru/C dose 5 g L^{-1})

Test no.	NaCl %	NaHCO$_3$[a] mM	Na$_2$SO$_4$ mM	NaNO$_3$[a] mM	Temp °C	pH	k_0 mM min^{-1} g$_{Ru}$$^{-1}$
Baseline condition							
1	5	100	100	100	30	No control	0.30 ± 0.03
Effect of solution pH							
2	0	0	0	100	30	7.5	0.09 ± 0.01
3	0	0	0	100	30	11	0.11 ± 0.01
Effect of salts							
4	0	0	0	100	30	No control	0.15 ± 0.01
5	0	100	0	100	30	No control	0.58 ± 0.01
6	10	100	200	100	30	No control	0.10 ± 0.01
7	5	0	100	100	30	No control	0.16 ± 0.03
Effect of initial nitrate concentration							
8	5	100	100	50	30	No control	0.70 ± 0.07
9	5	100	100	200	30	No control	0.08 ± 0.01
Effect of temperature							
10	5	100	100	100	25	No control	0.18 ± 0.01
11	5	100	100	100	35	No control	0.32 ± 0.04

[a]Amounts initially added.

fold increase in the concentrations of these two anions lowered the apparent rate constant by 37% compared with the baseline condition. These results are consistent with observations with Pd-based catalysts. More interestingly, addition of bicarbonate showed a positive effect on nitrate hydrogenation with Ru/C. For example, the apparent rate constant observed in solution containing both bicarbonate and nitrate was nearly four times higher than that observed in the absence of bicarbonate (entries no. 4 and 5 in Table 5.2). Also, when bicarbonate was eliminated from the baseline testing condition the apparent rate constant decreased by 62% (entry no.7 in Table 5.2). Positive effects of bicarbonate on nitrate reduction activity have only been reported when co-feeding CO_2 to maintain the solution acidity.[40, 41] Under conditions where the solution pH was maintained by adding HCl, higher concentration of bicarbonate led to reduced activity, similar to two other anions.[21] Therefore, the promoting effect of bicarbonate may be associated with its ability to donate proton:

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \qquad pK_a = 10.33 \qquad\qquad (5.3)$$

For example, under the baseline testing condition, the solution pH rose past the bicarbonate pK_a value in less than 2 h, suggesting significant dissociation of bicarbonate and consumption of protons. However, the impact of bicarbonate on reaction kinetics may cease to be positive with increasing bicarbonate concentration, because high concentration of negatively charged bicarbonate and carbonate ions can compete with nitrate for available catalyst surface sites.

Nitrate concentration was found to be an important factor for the reaction rate. Compared with the baseline condition, the nitrate reduction apparent zero-order rate constant increased with decreasing initial nitrate concentration (entries no. 8 and 9 in Table 5.2). Although the possibility of internal mass transfer limitation cannot be ruled out at this time, these observations are consistent with Langmuir-Hinshelwood model, a surface reaction model widely adopted for catalytic hydrogenation of oxyanions.[4, 37, 38, 42] The higher apparent rate constant at lower initial nitrate concentrations may result from inhibition of hydrogen adsorption at the higher concentrations of nitrate and its conversion intermediates.[4, 43] The surface reaction kinetic model considering reactants competition can be written as follows:

$$Rate = \frac{kK_{nitrate}C_{nitrate}K_{hydrogen}C_{hydrogen}}{(1+K_{nitrate}C_{nitrate}+K_{hydrogen}C_{hydrogen})^2} \qquad\qquad (5.4)$$

Where k is the rate constant for the surface reaction, $K_{nitrate}$ and $K_{hydrogen}$ are the adsorption equilibrium constants for nitrate and hydrogen, respectively, $C_{nitrate}$ is the aqueous concentration of nitrate, and $C_{hydrogen}$ is the aqueous concentration of hydrogen, which is proportional to hydrogen partial pressure in the gas phase according to Henry's law. Under the current testing

conditions, nitrate concentration is much higher than hydrogen ($K_{nitrate}C_{nitrate} \gg 1 \gg K_{hydrogen}C_{hydrogen}$), and Eq. 5.4 can be reduced to

$$\text{Rate} = \frac{kK_{hydrogen}}{K_{nitrate}} \frac{C_{hydrogen}}{C_{nitrate}} \tag{5.5}$$

Since k, $K_{nitrate}$, $K_{hydrogen}$, and $C_{hydrogen}$ are all constant, the reaction rate is expected to be inversely dependent on $C_{nitrate}$. The initial reaction rate, coincident with the apparent zero-order rate constant k_0, was roughly proportional to the inverse of the initial nitrate concentration (Figure D.2 in Appendix D), further confirming that surface hydrogen is at very low concentrations and limiting the reaction kinetics.

Temperature showed a positive effect on reaction rate (entries no. 10 and 11 in Table 5.2), and similar observations have been reported for nitrate reduction with Pd-based catalysts.[44, 45] Arrhenius plot of the apparent zero-order rate constant between 25-35 °C yielded an apparent activation energy of 45 ± 6 kJ mol^{-1}. This value is comparable with the apparent activity energy for nitrate hydrogenation with a Pd-Cu/Al$_2$O$_3$ catalyst.[46]

5.4.2 Ammonia recovery by membrane distillation

The membranes employed in membrane distillation process are hydrophobic, allowing vapor phase species to permeate while rejecting ionic constituents in the aqueous phase. Due to the relatively low temperature studied (no higher than 35 °C for all tests), water evaporation through the membranes was not expected to be significant during ammonia recovery. The concentration of H$_2$SO$_4$ in the acid adsorbent was designed to be excessive to ensure complete capture of ammonia as (NH$_4$)$_2$SO$_4$.

To study the reaction kinetics and identify important operating factors for membrane distillation, a similar research approach was employed to that used for catalytic hydrogenation

studies. Under the baseline testing condition, the feed was a synthetic solution whose composition was based on the baseline testing solution in catalytic hydrogenation assuming complete nitrate reduction to ammonia according to Eq. 5.1 without pH control. Feed temperature was 30 °C, same as the baseline testing condition in catalytic hydrogenation. Different flow rates were varied, and 1.5 L min^{-1} was chosen to achieve a high flux while maintaining the system at low pressure (7.5 psig) to minimize the risk of wetting the membranes.

Under the baseline condition, the kinetics of ammonia removal from the feed can be well described by a first-order rate law over the entire reaction time course (Figure 5.4a). The driving force for ammonia mass transfer is the difference between free ammonia concentration in the feed and that in the acid adsorbent. Under the baseline testing condition, the solution pH decreased from 11.2 to 10.8 due to the removal of a base (NH$_3$) from the solution.[47] In all but one test (entry no. 5 in Table 5.3), solution pH remained higher than 10.7, where free ammonia is the dominant species (>96%). It can also be assumed that free ammonia reacted immediately with sulfuric acid on the other side of the membrane to form ammonium sulfate, so the concentration of free ammonia in the acid adsorbent was practically zero. Therefore, the flux of ammonia transfer from the feed to the acid adsorbent can be represented by the following equation:

$$J_{NH3} = K C_{NH3,f} \qquad (5.6)$$

Where J_{NH3} is the mass flux of ammonia (gNH$_3$-N m^{-2} h^{-1}), K is the overall mass transfer coefficient (m h^{-1}), and $C_{NH3,f}$ is the concentration of ammonia in the feed (mgNH$_3$-N L^{-1}). The overall mass transfer coefficient comprises three resistances (i.e., feed liquid side boundary resistance, membrane resistance, and acid adsorbent side boundary resistance) and depends on the membrane and operating conditions.[48] Practically, the value of K can be determined by the following equation:[48-50]

$$K=\frac{V}{At}\ln\left(\frac{C_{NH_3,0}}{C_{NH_3,t}}\right) \tag{5.7}$$

Where V is the volume of the feed (m^3), A is the membrane area (m^2), $C_{NH3,0}$ is the initial

concentration of ammonia in the feed (mM), and $C_{NH3,t}$ is the ammonia concentration in the feed

at time t (h). By plotting $\ln(C_{NH3,0}/C_{NH3,t})$ over t, a straight line with the slope of KA/V can be

obtained, and subsequently K was found. The initial J_{NH3} was then calculated from Eq. 5.6.

Under the baseline condition, the initial J_{NH3} was 268 ± 3 gNH_3-N m^{-2} h^{-1} with the corresponding

K of 0.19 ± 0.01 m h^{-1}. Nitrogen balance of the membrane distillation system was closed by

measuring the total ammonia in the feed and the acid adsorbent (Figure 5.4b), suggesting that the

system was well sealed, and loss of ammonia in the void space in the system was negligible.

Since the efficiency of ammonia transfer strongly depends on system configuration and

membrane properties, it is challenging to directly compare the kinetic parameters observed in

this study with those reported in the literature. However, within the same system, the effects of

feed solution chemistry and operating conditions can be studied. The influence of operating
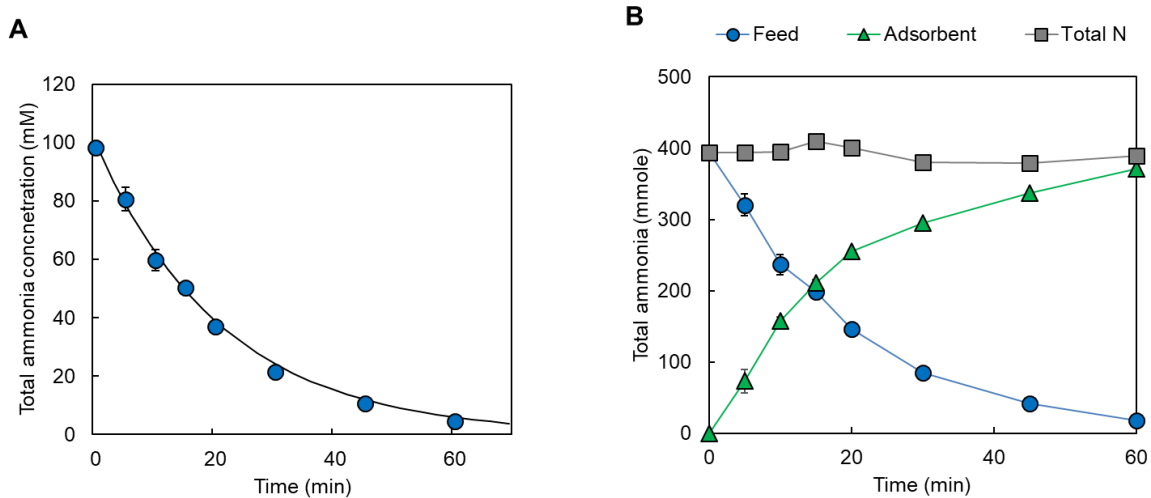
Figure 5.4 (A) Ammonia removal from brine by membrane distillation under baseline testing conditions. (B) Ammonia mass balance in feed and H_2SO_4 adsorbent solution. Solid line in (A) refers to the first-order rate law fit.

temperature was studied at three feed temperatures, i.e., 25 °C, 30 °C, and 35 °C. It was observed that ammonia removal kinetics (both K and initial J_{NH3}) increased 17% when increasing temperature from 25 °C to 30 °C (entries no. 1 and 2 in Table 5.3). Further increasing the temperature to 35 °C improved the kinetics by 22% (entry no. 3 in Table 5.3). This positive influence of temperature on ammonia removal efficiency is consistent with literature findings with various membrane distillation configurations such as vacuum and sweep gas membrane distillation.[51-53] On the other hand, using temperature to tune ammonia removal efficencity will be increasingly limited at higher temperature, because the mass transfer of water vapor is intensified due to higher water vapor pressure and diffusivity, resulting in reduced ammonia selectivity.[52]

Table 5.3 Summary of ammonia mass transfer coefficient (K) and initial mass flux (J_{NH3}) with different feed characteristics and operating conditions

Test no.	NaCl %	NaHCO$_3$[a] mM	Na$_2$SO$_4$ mM	Ammonia [ab] mM	Temp °C	Initial pH	Final pH[c]	K[b] m h^{-1}	Initial J_{NH3}[b] gNH$_3$-N m^{-2} h^{-1}
Baseline condition									
1	5	100	100	100	30	11.2	10.8	0.19 ± 0.01	268 ± 3
Effect of temperature									
2	5	100	100	100	25	11.2	10.9	0.16 ± 0.01	229 ± 3
3	5	100	100	100	35	11.2	10.7	0.23 ± 0.03	326 ± 37
Effect of salt									
4	0	100	0	100	30	11.6	11.3	0.19 ± 0.02	258 ± 21
5	10	100	200	100	30	11.1	10.7	0.18 ± 0.02	258 ± 26
Effect of solution pH and ammonia concentration									
6	5	50	100	50	30	11.1	10.7	0.20 ± 0.03	141 ± 21
7	5	200	100	50	30	9.2	9.1	0.10 ± 0.01	71 ± 1
8	5	50	100	200	30	12.7	12.6	0.16 ± 0.02	457 ± 49
9	5	200	100	200	30	11.5	11.0	0.17 ± 0.01	482 ± 39

[a]Amounts initially added.
[b]Calculated by using total ammonia concentration.
[b]Operation time 1h.

The impact of salts was studied by controlling the concentrations of NaCl and Na$_2$SO$_4$ in the feed solutions. Tests demonstrated that large variations in concentrations of these salts (0-10 wt% for NaCl, 0-200 mM for Na$_2$SO$_4$) had little influence on rates of ammonia removal from the

brine (entries no. 4 and 5 in Table 5.3). It has been reported that the solution ionic strength has slightly negative effect on the fraction of free ammonia species by increasing ammonium dissociation constant at higher ionic strength.[54] However, at the relatively high pH (>10.7) used in these tests, the fraction of free ammonia species remained high, rending the effect of ionic strength negligible.

Two factors, solution pH and initial ammonia concentration, were inherently coupled due to the hydroxide generated when simulating nitrate reduction to ammonia Eq. 5.1 In addition, the solution pH was also influenced by the buffering capacity of the solution during catalytic hydrogenation. Therefore, four tests were designed, combining two factors relevant to solution pH, i.e., initial nitrate concentration and bicarbonate concentration, each at two levels. Because we have assumed complete nitrate hydrogenation according to Eq. 5.1 and no loss of ammonia to the gas phase, the initial nitrate concentration in the feed to catalytic hydrogenation equals the initial ammonia concentration in the feed to membrane distillation. At low initial nitrate concentration (50 mM), the feed pH varied dramatically depending on the concentration of bicarbonate (entries no. 6 and 7 in Table 5.3). A low bicarbonate concentration (50 mM) led to a higher solution pH and K similar to values measured under the baseline testing condition. At higher bicarbonate concentration (200 mM), on the other hand, the brine was buffered more strongly during nitrate hydrogenation, resulting in an apparent solution pH of 9.2 in the membrane distillation feed, a condition wherein only ~50% of the ammonia is present as the free ammonia species. The mass transfer coefficient K (calculated by using total ammonia concentration) decreased 51% compared to that at low bicarbonate concentration. When the initial nitrate concentration was equal to or greater than the initial bicarbonate concentrations (entries no. 8 and 9 in Table 5.3), the solution pH of the ammonia product solution used as

membrane distillation feed was high (>11), leading to K values comparable with that measured at the baseline testing condition. Therefore, solution pH is a critical factor for ammonia recovery by membrane distillation. The initial J_{NH3} also increased with the initial ammonia concentration as expected from Eq. 5.6.

5.4.3 Ion exchange waste brine nitrate removal and nitrogen recovery

Based on findings with synthetic brine solutions, we then demonstrated nitrate removal and nitrogen recovery from a real ion exchange waste brine (Table 5.1 and Table 5.4) obtained from a California water utility. Kinetics of nitrate hydrogenation with Ru/C in the waste brine can be characterized by the zero-order rate law (Figure 5.5), and the apparent zero-order rate constant normalized to Ru mass was found to be significantly higher (1.80 ± 0.04 mM min^{-1} g$_{Ru}^{-1}$) than those measured in synthetic brines (Table 5.2). As a control, a synthetic waste brine was prepared with the same concentrations of major anions (chloride, nitrate and sulfate), alkalinity (by adding sodium bicarbonate), and initial solution pH (adjusted with NaOH) as the real waste brine. Experiments revealed a lower rate of nitrate hydrogenation in the synthetic waste brine than in the real waste brine (Figure 5.5), with the apparent zero-order rate constant ~30% lower (1.24 ± 0.02 mM min^{-1} g$_{Ru}^{-1}$). The origin of the higher activity observed in the real waste brine is unclear at this time, but the results support the technical feasibility of applying Ru/C for nitrate hydrogenation in ion exchange waste brine. Further research is needed to identify the cause of faster kinetics in the real waste brine, but it is noteworthy that the real waste brine contains several cations in addition to Na$^+$ (Table 1), the sole cation used in preparation of the synthetic waste brine. Divalent and trivalent cations (e.g., Ca^{2+}, Mg^{2+}) have been shown previously to enhance rates of nitrate hydrogenation.[29] In addition, the real waste brine contains a number of
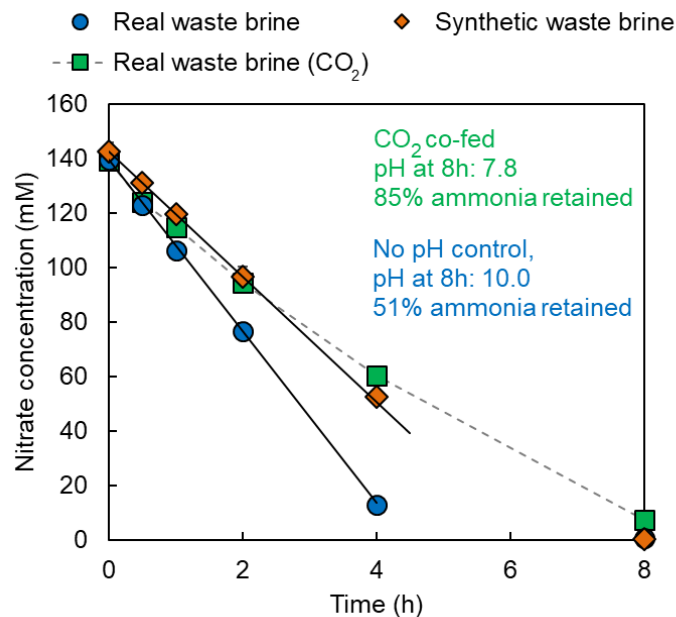
Figure 5.5 Catalytic nitrate hydrogenation in real waste brine and synthetic waste brine prepared with similar anionic composition. Conditions: 6 g L^{-1} Ru/C, 30 °C, no solution pH control, 1 atm H_2 headspace maintained by flowing H_2 at ca. 300 mL min^{-1}. The effect of pH control by flowing CO_2 (at ca. 65 mL min^{-1}) was also examined. Error bars indicate standard deviation from duplicate measurements (smaller than symbol if not visible). Solid line refers to the zero-order rate law fit.

minor constituents, including organics and trace metals (Table 5.1), which may interact with catalyst surfaces to promote nitrate enhanced reactivity.[55-57]

Considering that bicarbonate has shown positive influence on nitrate hydrogenation kinetics (Table 5.2), tests were conducted to co-feed CO_2 with H_2, which is a common practice for solution pH control when treating nitrate with Pd-based catalysts.[21, 22] The nitrate hydrogenation rate was comparable with that in the absence of CO_2 in the initial 0.5 h, but the rate gradually decreased with reaction time (Figure 5.5). This observation could be a result of lower hydrogen partial pressure and the accumulation of bicarbonate over time. For example, the inorganic carbon concentration increased from 238 mM to 466 mM after 12 h of treatment. On the other hand, co-feeding CO_2 maintained solution pH between 7.6-7.9 and significantly improved retention of ammonia in the open reactor system. After 8 h of reaction, 85% of the

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Table 5.4 Water quality comparison of initial real waste brine, brine solution after treatment with Ru/C, and solution after membrane distillation.

Solution chemistry	Real waste brine	After hydrogenation	After membrane distillation
pH	8.5	8.6	9.9[a]
Cl^-	13,685 mg L^{-1} (2.3 wt% as NaCl)	14,198 mg L^{-1} (2.3 wt% as NaCl)	14,204 mg L^{-1} (2.3 wt% as NaCl)
HCO_3^- and CO_3^{2-}	232 mM	485 mM	484 mM
NO_3^-	9,262 mg L^{-1} (149 mM)	79 mg L^{-1} (1.2 mM)	75 mg L^{-1} (1.2 mM)
SO_4^{2-}	4,346 mg L^{-1} (45 mM)	4,515 mg L^{-1} (47 mM)	4,283 mg L^{-1} (45 mM)
Total ammonia	<3.2 mM (detection limit)	136 mM	9 mM

[a]Solution pH was adjusted to 10.0 by adding NaOH prior to membrane distillation

ammonia was retained in the liquid phase when co-feeding CO_2 compared to only 51% in the absence of CO_2 buffer.

Catalytic hydrogenation of real waste brine was scaled up in 1 L graduated glass bottle to provide feed solution for membrane distillation. Reactor design likely affects reaction kinetics, but its optimization is beyond the scope of this study, and the reaction was conducted up to 24 h while co-feeding CO_2 to enhance ammonia retention in the liquid phase. These conditions resulted in near complete nitrate hydrogenation, and the liquid phase retained 91% of the ammonia reaction product (Table 5.4). Prior to membrane distillation, the solution pH was adjusted to ~10.0 with NaOH to reflect the pH conditions observed when pH was allowed to drift without CO_2 buffer.

Kinetics of ammonia removal from the catalytically treated real waste brine can be characterized by a first-order rate law (Figure 5.6a), with K and initial J_{NH3} being 0.11 m h^{-1} and 199 gNH$_3$-N m^{-2} h^{-1}, respectively (uncertainty not reported due to lack of duplicate experiment of limited real waste brine supply). These observations are qualitatively consistent with results obtained with synthetic solutions prepared to mimic the major waste brine components. Nitrogen

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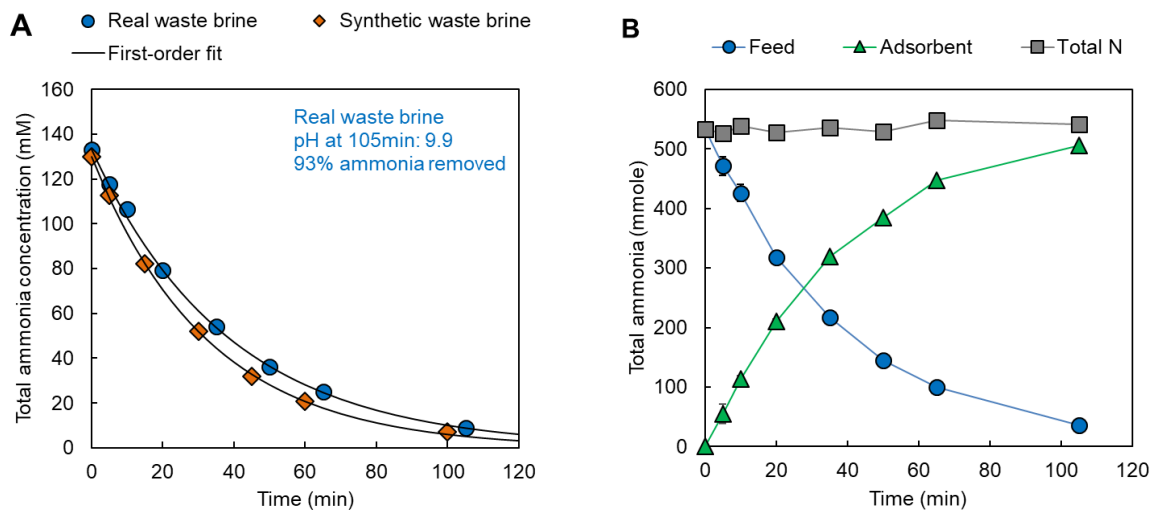
Figure 5.6 (A) Ammonia removal from real waste brine and synthetic solution by membrane distillation. Conditions: 4 L feed at 1.5 L min^{-1}, 1.15 L 0.25 M H_2SO_4 adsorbent solution at 1.5 L min^{-1}, 30 °C. (B)Ammonia mass balance in real waste brine feed and H_2SO_4 adsorbent solution. Solid line in (A) refers to the first-order rate law fit.

balance was also well closed by measuring the total ammonia in the feed and the acid adsorbent solution (Figure 5.6b). Salt composition and concentrations after membrane distillation were almost invariant (Table 5.4), verifying the membrane integrity during the experiment and high selectivity to ammonia for mass transfer. Similar to the study of catalytic hydrogenation, a synthetic waste brine was prepared with the same concentrations of major anions (chloride, bicarbonate, and sulfate), total ammonia concentration, and initial solution pH (adjusted with NaOH) as the real waste brine. Ammonia removal K (0.12 ± 0.01 m h^{-1}) and initial J_{NH3} (225 ± 4 gNH_3-N m^{-2} h^{-1}) for in the synthetic waste brine were similar to values measured in the real waste brine. These results suggest membrane distillation is effective at recovering ammonia from real waste brine. Potential membrane fouling from continuous treatment of real waste brine and its impact on ammonia recovery efficiency need to be future evaluated at longer operation timescale.

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The overall nitrogen recovery from the real waste brine through the hybrid catalytic hydrogenation/membrane distillation process is 79%, validating the use of this process for efficient nitrogen resource recovery from waste ion exchange brines.

5.4.4 Application considerations of the hybrid process

Conceptual evaluation of the economic and environmental viability of the hybrid catalytic hydrogenation/membrane distillation process may be achieved by comparing with a more developed brine treatment system using Pd-based catalysts.[21, 22] Previous work showed that both the O&M costs and environmental impacts of recycling ion exchange brines by treating nitrate with Pd-In/C catalysts can be lower than those of conventional ion exchange processes.[21] A critical factor to delivering these benefits is reducing the catalyst cost, particularly the use of Pd.[58] Catalyst cost is directly associated with the cost of the active metal (dominated by Pd for Pd-In/C catalysts) and catalyst activity. Less catalyst material is required for catalysts that exhibit higher activity. Along this line of consideration, Ru catalysts have an advantage over Pd-based catalysts due to the historically lower cost of Ru.[4, 36, 59] In addition, Ru catalysts have been reported to have high activity for nitrate reduction, similar to Pd-Cu/C catalysts.[3] This study further confirmed that Ru/C is active for nitrate hydrogenation in various brine conditions. Although activity comparison between Ru/C determined in this study and literature reported values for Pd-In/C catalysts is not straightforward due to difference in reaction conditions, their metal mass-normalized apparent zero-order rate constants are of similar magnitude when treating synthetic waste brines, and the rate constant with Ru/C for treating a real waste brine is approximately two-fold higher than the highest value reported for Pd-In/C catalysts,[21, 22] all suggesting that Ru catalysts have a potential to improve the economic and environmental sustainability of the catalytic treatment step of the hybrid process.

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A less often studied, but critically important consideration, for catalytic processes is catalyst stability and longevity. Catalyst longevity is ultimately required to fulfill the assumptions of catalyst lifetime (usually years) during techno-economic analysis and/or life cycle assessment.[21, 23, 59] Catalyst stability also affects catalyst loading design for a fixed volume of water brine and vice versa, brine regeneration cycle design with a fixed loading of catalyst. Generally, the higher the total volume of waste brine that can be treated with the same catalyst, the more savings that can be gained from brine reuse.[22] Ru/C stability for waste brine hydrogenation was initially assessed using a batch recycle test. After the first use, catalyst activity increased in the following cycles (Figure 5.7). This increase in activity is likely related to catalyst activation. As shown in a previous study, elevated temperature in either inert or reducing gas environment improved the activity of the commercial Ru/C by desorbing synthesis residue and exposing redox-labile Ru species.[4] ICP analysis of the filtrate from catalyst collection detected trace amounts of Ru (<0.2% of the total amount of Ru). However, it is unclear whether the detected Ru resulted from metal dissolution or the release of loosely bound Ru nanoparticles from attrition. These results demonstrated that Ru/C can be recycled in a semi-batch reactor, and catalyst deactivation through leaching or fouling is insignificant within four use cycles. Further study, ideally in continuous flow reactors, is required to evaluate the longer-term stability of Ru/C during waste brine treatment applications.

Compared with previous brine treatment systems, the hybrid catalytic hydrogenation/membrane distillation process enables nitrogen recovery, providing potential economic and environmental benefits in addition to reduced salt consumption. When considering the entire process for source water treatment (Figure 5.1), nitrogen in the form of dilute nitrate was transformed to a much more concentrated $(NH_4)_2SO_4$ aqueous solution, which can be used

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as a liquid fertilizer or a precursor for solid fertilizer.[33-35] This process likely has higher energy efficiency compared to the traditional Haber–Bosch ammonia synthesis process that demands high temperature and pressure, because it requires minimal thermal energy; instead, it leverages chemical potential difference as the driving force (e.g., nitrate adsorption to ion exchange resin, nitrate hydrogenation on Ru surface, and ammonia mass transfer across membrane). A detailed techno-economic analysis is required to estimate the minimum selling price of the brine-derived $(NH_4)_2SO_4$ product.
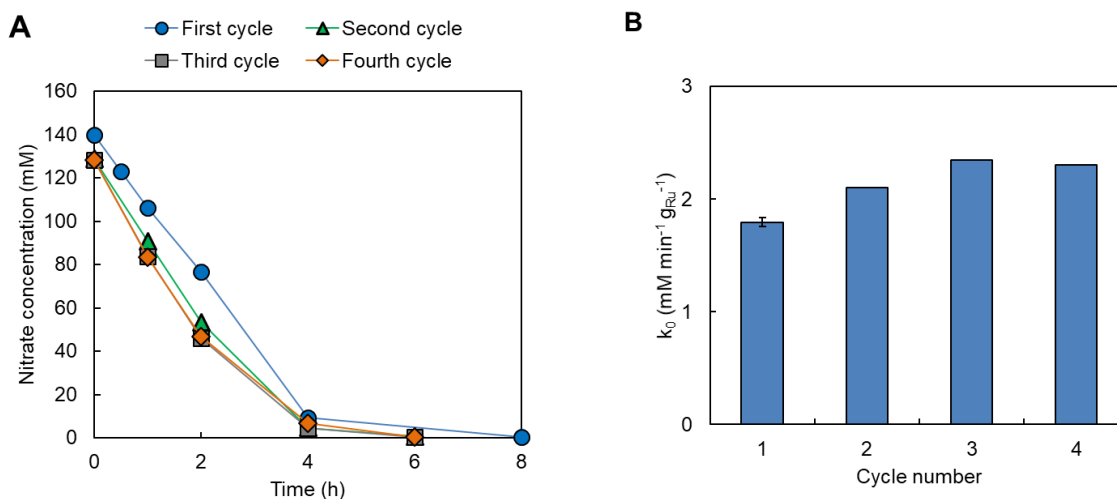
Figure 5.7 Ru/C reused for three reaction cycles in real waste brine: (a) nitrate hydrogenation time courses, and (b) apparent zero-order rate constants. Conditions: 6 g L^{-1} Ru/C, 30 °C, no solution pH control, 1 atm H_2 headspace maintained by flowing H_2 at ca. 300 mL min^{-1}, catalyst dried at 70°C in between reuse cycles.

To meet the increasing demand for fertilizer,[34] the yield of the ammonium sulfate should be maximized, which depends on the nitrogen recovery efficiency of the catalytic hydrogenation/membrane distillation process. As shown in Figure 5.7, in the absence of pH control, solution pH rose beyond the pK_a of NH_4^+ and accelerated ammonia loss to the flowing H_2. To better understand the dynamics of ammonia formation and volatilization, the total ammonia concentration was monitored during waste brine hydrogenation (Figure 5.8a). Initially,

total ammonia concentration increased with nitrate hydrogenation. When nitrate conversion was near complete, total ammonia concentration began to decrease. Gas-liquid partition of NH_3 led to a decreasing total nitrogen concentration with time. Therefore, liquid phase ammonia retainment can be improved by controlling the reaction time. For example, at 4 h the ammonia retainment retention was 70%, 39% higher than that observed at 8 h. However, it came with the trade-off of incomplete nitrate conversion. With flowing CO_2 as a pH buffer, ammonia retainment can be improved by maintaining the solution pH below the pK_a of NH_4^+. Even at this low pH (7.8), the slow and steady loss of ammonia was still observed (Figure 5.8b). Instead of semi-batch reactor, a completely enclosed batch reactor may be used to curb the loss of ammonia to the flowing H_2 and/or CO_2. The key to the batch reactor design is minimizing the reactor size while ensuring sufficient hydrogen supply, which may require a pressurized system. Increasing the hydrogen pressure can also enhance nitrate hydrogenation kinetics as discussed before and potentially improve hydrogen and Ru utilization efficiency, leading to reduced cost and environmental impact.[21, 22]

Membrane distillation (or membrane contactor) has been considered a cost effective, energy efficient technology for removing ammonia from industrial and agricultural wastewater.[52, 60] This study demonstrated its successful application to recovering ammonia from ion exchange waste brine at high efficiency under ambient temperatures. The high ammonia removal efficiency is attributed to several factors including the large membrane surface area and high feed solution pH. As nitrate hydrogenation produces hydroxide to raise solution pH, the membrane distillation process can benefit from an upstream catalytic reactor operated without pH control, which also saves the cost on alkali for adjusting pH for membrane distillation. In addition to the aforementioned pressurized batch reactor, optimization of the existing system,

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such as directing the H_2 flow to the acid adsorbent, can be explored to maximize ammonia recovery. Alternative membrane distillation should be assessed to further improve unit efficiency and reduce membrane cost.[61] A major concern during membrane distillation implementation is membrane fouling, such as by particulate and organics.[48, 62, 63] The risk of particulate fouling caused by catalyst particle can be reduced by filtration, which is also an effective method for removing scalants precipitated at high solution pH (e.g., calcium carbonate). Organic fouling is less of a concern for the ion exchange waste brine due to its low organic carbon content (Table 5.1), but the accumulation of organic carbon over several brine regenerant cycles may lead to fouling over long-term operation and needs to be evaluated.
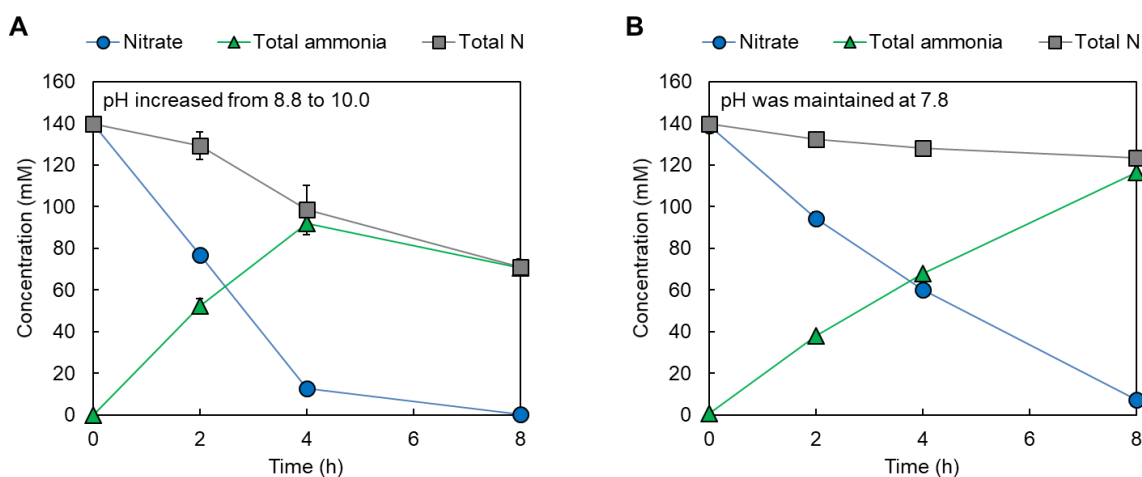
Figure 5.8 Aqueous concentration of nitrate and total ammonia during real waste brine catalytic hydrogenation: (a) no pH control (b) pH maintained by flowing CO_2. Conditions: 6 g L^{-1} Ru/C, 30 °C, 1 atm H_2 headspace maintained by flowing H_2 at ca. 300 mL min^{-1}, in (b) CO_2 flow at ca. 65 mL min^{-1}. Error bars indicate standard deviation from duplicate measurements (smaller than symbol if not visible).

5.5   Conclusions

This work demonstrated a hybrid catalytic hydrogenation/membrane distillation process that potentially enables ion exchange waste brine reuse and captures nitrogen in the form of potential fertilizer product. A commercial Ru/C catalyst, much lower in cost than widely studied

Pd-based catalysts, was found to be active for nitrate reduction to ammonia in real and synthetic waste brine matrices. In a well-mixed semi-batch reactor, nitrate hydrogenation with Ru/C exhibited zero-order kinetics, and nitrate was hydrogenated to ammonia at high selectivity. Further, the resulting ammonia product could be efficiently recovered as $(NH_4)_2SO_4$ by membrane distillation. The mass transfer efficiency was favored by high solution pH and temperature and not affected by salt composition or concentration in the waste brine solution. The hybrid process was finally applied to a real ion exchange waste brine and demonstrated high nitrate hydrogenation and ammonia recovery efficiency. Further studies are needed to evaluate alternative reactor designs for improving nitrate hydrogenation kinetics and overall ammonia recovery and to evaluate the reuse of treated brines for regeneration ion exchange resins.

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CHAPTER 6

TAILORING DIESEL BIOBLENDSTOCK FROM INTEGRATED CATALYTIC
UPGRADING OF CARBOXYLIC ACIDS: A "FUEL PROPERTY FIRST" APPROACH

A modified version of this chapter was submitted to *Energy & Environmental Science*

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6.1   Abstract

Lignocellulosic biomass offers the potential to produce renewable fuels at a scale

commensurate with petroleum consumption. Hybrid approaches that combine biological and

chemocatalytic processes have garnered increasing attention due to their flexibility for feedstock

utilization and diversity of potential products. Of note, lignocellulosic sugars can be converted

biologically to short-chain carboxylic acids, while subsequent chemocatalytic upgrading can

elongate the carbon backbone and remove oxygen from the structure to produce drop-in

hydrocarbon fuels. However, hybrid conversion processes are typically not designed with the

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fuel properties in mind *a priori*. In this work, we apply a "fuel property first" design approach to a tailored hydrocarbon diesel bioblendstock. Initially, model predictions for six fuel properties critical to diesel applications were used to screen an array of hydrocarbons accessible from upgrading individual and mixed C_2/C_4 acids. This screening step allowed for down-selection to a non-cyclic branched C_{14} hydrocarbon (5-ethyl-4-propylnonane) that can be synthesized from butyric acid through sequential catalytic reactions of acid ketonization, ketone condensation, and hydrodeoxygenation. Following evaluation of each conversion step with model compounds, butyric acid was then converted through an integrated catalytic process scheme to achieve >80% overall carbon yield to a hydrocarbon mixture product containing >60% of the target C_{14} hydrocarbon. The potential of this conversion strategy to produce a hydrocarbon diesel bioblendstock from lignocellulosic biomass was then demonstrated using corn stover-derived butyric acid produced from *Clostridium butyricum* fermentation. Experimental fuel property testing of the purified C_{14} blendstock validated the majority of the fuel property model predictions. Meanwhile, the crude conversion product met fuel property target metrics, validating conversion process development. When the C_{14} bioblendstock was blended into a petroleum diesel at 20 vol.%, the blend maintained low cloud point, high energy density, and cetane number. Notably, the blend reduced sooting tendency by more than 10%, highlighting the potential of the tailored bioblendstock to reduce particulate emissions.

6.2   Introduction

Biofuels have the potential to offset environmental impacts of the transportation sector, which accounts for 55% of oil consumption and 23% of energy-related CO_2 emissions globally.[1,2] Passenger vehicles rank number one in consumption of oil, closely followed by road freight vehicles. Due to technology advances such as electrification, oil demand for passenger vehicles

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has begun to plateau, but the demand of oil (primarily diesel) for road freight vehicles is projected to continue rising over the next few decades.[3] Therefore, identifying routes to sustainable diesel fuel production is particularly important to both meeting future demand and curbing climate change. Lignocellulosic biomass is a relatively low-cost feedstock that allows renewable fuels to be produced at a meaningful scale.[4] A wide array of molecules can be accessed from lignocellulosic biomass through diverse conversion pathways (e.g., biochemical, thermochemical, hybrid),[5-7] creating ample opportunities to produce biofuels. A rational fuel design approach can have a major impact on enhancing the value proposition of biofuels.

Computational tools have seen growing application in multiple product development fields to reduce time, manpower, and cost.[8-10] For example, computer-aided molecular design leverages quantitative structure–property relationships (QSPRs) and numerical optimization algorithms to search for optimal molecular structures across massive design space that includes completely novel structures.[11] In the context of biofuel design, computational fuel property prediction can be employed to screen potential fuel molecules and select a subset of the most promising candidates for further experimental study.[12, 13] This process is enabled by fuel property predictive models, which provide estimates of fuel characteristics relevant to its handling and application, such as physical and chemical properties (e.g., density, boiling point, and C/H/O composition). Models specifically related to fuel performance have received increasing attention and can provide valuable information for designing performance-advantaged fuel molecules. These include octane number (ON), cetane number (CN), and yield sooting index (YSI), which describe fuel antiknock quality, autoignition ability, and sooting tendency, respectively.[14, 15]

Hybrid conversion routes integrating biochemical and chemocatalytic processes provide numerous routes to access promising fuel molecules from biomass. Of note, short-chain

carboxylic acids can be produced from the low-cost anaerobic fermentation of lignocellulosic sugars and waste streams in high yield.[16-20] Although acids cannot be used directly as fuel due to their low energy density and corrosive nature, the functionality of the carboxylic acid group allows for diverse chemocatalytic chemistries to extend the carbon chain length and reduce oxygen content. For example, recent efforts have identified catalysts and reaction parameters for converting carboxylic acids to ketones, alcohols, and hydrocarbons of higher carbon number and diverse connectivity (e.g., linear, branched, cyclic) through a combination of C-C coupling, dehydration, and hydrogenation chemistries.[21-24] However, the viability of the conversion products as biofuel has not be evaluated. Efficient evaluation of these fuel candidates can be facilitated by computational tools, which remain underutilized.

To address these gaps, we demonstrate a "fuel property first" design approach to identify, synthesize, and experimentally confirm the fuel properties of promising hydrocarbon molecules derived from short-chain carboxylic acids to serve as drop-in diesel bioblendstocks (Figure 6.1). Initially, we mapped the potential array of long-chain hydrocarbon molecules accessible from the catalytic upgrading of acetic and butyric acid. The hydrocarbon functionality was targeted to take advantage of its compatibility with existing fuel infrastructure that would allow it to be deployed in the near term as a drop-in blendstock.[25, 26] Fuel property prediction tools were then used to screen and down-select target molecules for further conversion pathway development. The catalytic conversion efficiency and product yield were evaluated for both single-step conversion and integrated catalytic process scheme using butyric acid, and this integrated scheme was then demonstrated using butyric acid derived from the anaerobic fermentation of corn stover hydrolysate. Lastly, fuel property testing evaluated both the neat blendstock and 20 vol.% blend

fuel properties. Results from this work provide justification for future process scale-up and fuel performance evaluation.
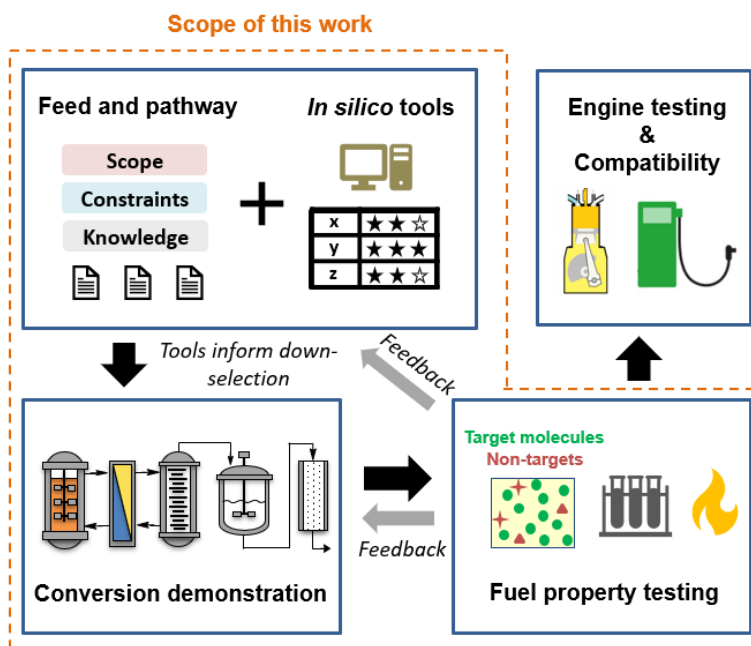
Figure 6.1 "Fuel property first" design approach to leverage fuel property predictive models for the design of performance-advantaged diesel bioblendstock.

6.3   Results

6.3.1   Fuel property prediction

6.3.1.1 Mapping hydrocarbons derived from C2/C4 acids

Fermentation-derived acetic acid and butyric acid were selected for combinatorial screening since they can be anaerobically produced from mixed lignocellulosic sugars in high yields.[17, 27] Hydrocarbons with potential to be generated from upgrading individual and mixed C_2/C_4 carboxylic acids were then mapped using a multi-step catalytic conversion route consisting of ketonization, condensation, and hydrodeoxygenation (HDO) (Figure 6.2). Ketonization reacts two carboxylic acids to extend their carbon chain-length by forming a ketone with the release of CO_2 and H_2O.[28, 29] Self-ketonization of acetic acid and butyric acid generates acetone and 4-

heptanone, respectively, while cross-ketonization between these two acids generates 2-pentanone. The ketone carbon backbone can be further elongated by condensation reactions that form non-cyclic branched dimers and cyclic trimers, while fully retaining all carbon and releasing oxygen in the form of water.[30] Lastly, HDO converts condensation products to hydrocarbons, with dimers resulting in non-cyclic branched hydrocarbons and trimers resulting in cyclic hydrocarbons.[21, 24, 30] Overall, the reaction mapping process resulted in 30 hydrocarbons spanning from C_6 to C_{21} (Table E.1 in Appendix E). While most of these hydrocarbons displayed carbon numbers within the range of diesel fuel (C_{10} to C_{25}),[31] their fuel properties were evaluated computationally to determine their dependence on molecular structure.
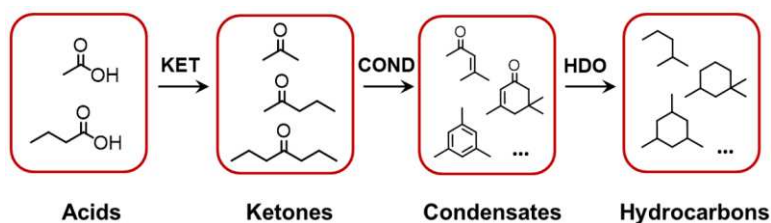
Figure 6.2 Upgrading scheme for converting C_2/C_4 carboxylic acids to hydrocarbon molecules via ketonization (KET), condensation (COND), and hydrodeoxygenation (HDO).

Fuel properties of the hydrocarbons were estimated using predictive models and compared against target metrics to identify desirable molecules and structures. These properties concern multiple aspects of fuel deployment, including physicochemical requirements, energy content, safety considerations, and emission potential. Starting with low-temperature handling ability, a fuel with an adequate regional and seasonal applicability requires a low melting point (or low cloud point for mixtures). A maximum value of 0 °C was used for initial screening.[32] Using predictive models based on group contribution and correlation,[33, 34] the non-cyclic branched hydrocarbons were all anticipated to exhibit low melting points (<-30 °C) suitable for cold environments, while cyclic hydrocarbons of C_{15} or larger risk failing to meet the

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requirement. Similarly, efficient fuel utilization must also satisfy a boiling point requirement, because non-volatile compounds resist evaporation/burning and remain in-cylinder, causing long-term operation issues. This fuel criterion was defined to be <338 °C, consistent with the maximum allowable T90 specified for petroleum diesel by ASTM D975.[35] Except for C_{21} molecules, group contribution methods[33, 34, 36] predicted that all of the hydrocarbons evaluated herein meet this requirement. Meanwhile, low boiling point compounds cause safety concerns because they may form a flammable fuel-air mixture above the liquid. To ensure the safe handling and storage of a fuel, a minimum flash point of 52 °C is specified for general purpose diesel by ASTM D975 and employed as a screening criterion in current study.[35] Molecules of C_{11} and above in both non-cyclic branched and cyclic hydrocarbon groups were predicted to meet this requirement using correlations built from fuel and hydrocarbon databases,[37, 38] Generally, a positive trend with carbon number was observed for these three fuel properties (Figure E.1a-c in Appendix E), as expected for paraffinic hydrocarbons.[39-41]

Energy density, which is essential to fuel economy, was quantified by the lower heating value (LHV) of each compound. This is a measure of the heat released by combusting a quantity of fuel, minus the heat of vaporization of the combustion-generated water. LHV varies between 32-44 MJ kg^{-1} for petroleum diesel, and a value of 40 MJ kg^{-1} was selected as the minimum requirement to ensure a competitive energy density. Utilizing models correlating heats of combustion with elemental analysis,[42-44] all mapped hydrocarbon molecule predictions fell well above the LHV requirement and were nearly uniform (Figure E.1d in Appendix E) due to similarities in elemental composition (e.g., 84-86 wt% carbon).

The autoignition and sooting behavior of the hydrocarbons were informed by predicting CN and YSI using machine learning methods.[45-47] For CN, a higher value indicates faster

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autoignition, which in turn can improve heat release rates and engine cold-start capabilities. The minimum requirement of 40, in line with ASTM D975 requirements, was selected to ensure adequate fuel reactivity,[35] although CN requirements can vary depending on the region (e.g., a minimum CN of 51 required by DIN EN 590 in Europe[48]). Nine non-cyclic branched hydrocarbon molecules and two cyclic hydrocarbon molecules were predicted to meet the minimum requirement of 40 (Table E.1 in Appendix E). Previous studies have shown that CN increases with the secondary C-H:primary C-H ratio due to a lower-energy alkylperoxy radical isomerization pathway enabled by secondary C-H bonds.[49-51] However, the absence of a strong correlation in this study (Figure E.1e in Appendix E) suggested significant influence from tertiary C-H and/or quaternary carbon as well.[52]
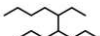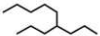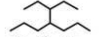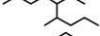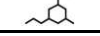
In contrast to autoignition ability, soot emission from diesel combustion currently does not have a known verified predictive fuel property metric. Diesel combustion is largely mixing-controlled, and soot formation is likely to depend on intrinsic sooting tendency, ignition delay, and physical properties relative to spray penetration and breakup. For this initial screening, YSI was chosen to assess the sooting potential of fuel candidates, with the higher value denoting stronger chemical sooting tendency.[47] Predicted YSI of the mapped hydrocarbons was shown to generally increase with carbon number in (Figure E.1f in Appendix E). YSI normalized by carbon number characterizes the average contribution of each carbon atom in the molecule to soot formation and was roughly constant for each category of hydrocarbons (see last column of Table E.1 in Appendix E). For the non-cyclic branched hydrocarbons, normalized YSI values varied between 5.9–6.8 and were lower than those of the cyclic hydrocarbons (7.3–9.0). The stronger sooting tendency of the cyclic structure agrees with experimental observations in the

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literature,[15] as small cyclic hydrocarbons tend to have lower energy barrier pathways towards forming resonantly-stabilized soot precursors.[53]

6.3.1.2 Down-selection of targets for diesel blendstock

Based on these predicted fuel properties, a subset of C_{12}–C_{14} molecules was identified to contain promising diesel candidates, including four non-cyclic branched hydrocarbon molecules and one cyclic hydrocarbon molecule (Table 6.1). These molecules are accessed from either single C_4 acid or mixed C_2/C_4 acids. With butyric acid, the C_{14} hydrocarbon in Table 6.1 can be synthesized from self-condensation of 4-heptanone that is generated from butyric acid ketonization. When mixed C_2/C_4 acids are used, acetone and 2-pentanone are formed in addition to 4-heptanone, which provides a pathway to all five of the down-selected molecule candidates. However, the presence of acetone and 2-pentanone negatively impacts the ability to selectively produce the target hydrocarbon molecules due to their facile condensation into cyclic trimers that react to form cyclic hydrocarbons after HDO.[21, 24, 30] As noted, the resulting cyclic hydrocarbons display less desirable diesel fuel properties, such as low CN and high YSI. Therefore, we chose to focus on the conversion pathway that starts solely with butyric acid targeting the non-cyclic

Table 6.1 Model predictions of melting point, boiling point, flash point, lower heating value (LHV), cetane number (CN), and yield sooting index (YSI, normalized to carbon number in parentheses) for down-selected hydrocarbon molecules. Average values reported when multiple predictions are available. Full list of molecule candidates and model predictions provided in Table E.1 in Appendix E.

Hydrocarbons	C No.	Melting point (°C)	Boiling point (°C)	Flash point (°C)	LHV (MJ kg^{-1})	CN	YSI
Screening criteria	None	<0	<338	>52	>40	>40	None
	14	-38	241	82	45	48	91 (6.5)
	12	-48	204	62	45	45	71 (5.9)
	12	-61	199	61	45	44	75 (6.2)
	12	-61	199	61	45	43	75 (6.2)
	13	-24	231	84	45	44	99 (7.6)

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branched C_{14} hydrocarbon, 5-ethyl-4-propylnonane, shown in the first entry of Table 6.1. Previous studies have shown proof-of-concept for the individual catalytic conversion steps comprising this pathway.[24, 30] As such, this work looked to evaluate the integrated catalytic conversion scheme and validate diesel blendstock properties for both the target C_{14} hydrocarbon and crude conversion product.

6.3.2 Catalytic upgrading of butyric acid

6.3.2.1 Single step conversion of model compounds

Initially, each catalytic conversion step in the butyric acid upgrading scheme was evaluated individually for conversion efficiency and carbon yield with the aim of moving towards process relevant conditions. The ketonization reaction was first performed using commercial butyric acid (≥99% purity, Sigma Aldrich) in a continuous flow reactor to remove the corrosive acid functional group and increase the C_4 carbon chain length to C_7, producing CO_2 and water in the process. The reactor was packed with a commercial ZrO_2 catalyst, which is an amphoteric redox metal oxide known to provide high activity and selectivity for this chemistry.[54] The catalyst displayed a surface area of 65 m^2 g^{-1} and total acidity of 163 µmol g^{-1} (Table E.2 in Appendix E). At 435 °C and a weight hourly space velocity (WHSV) of 3.8 h^{-1}, butyric acid was completely converted for over 11 hours of time-on-stream with an overall mass recovery >92% (Figure 6.3). The gas phase product was primarily CO_2, and the condensable liquid product was biphasic due to the low water solubility of 4-heptanone (approx. 3 g L^{-1} at room temperature). The purity of 4-heptanone in the organic liquid phase was 90%. Although the non-target products were not fully identified, work was conducted to determine the impact of these compounds on the integrated catalytic upgrading steps and final fuel properties, as discussed below.
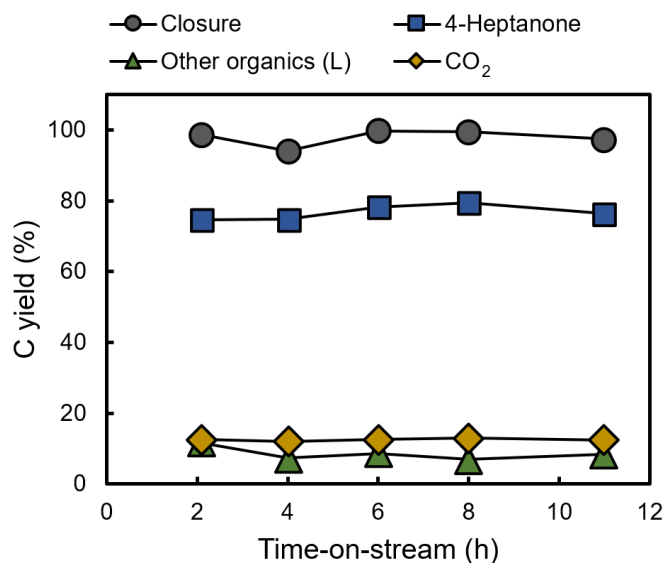
Figure 6.3 On-stream performance and product distribution of commercial butyric acid ketonization over 3 g ZrO_2 in flowing Ar [1 atm, 100 mL (STP) min^{-1}] at 435 °C and WHSV = 3.8 h^{-1}. WHSV was calculated using the mass flow rate of butyric acid and the mass of the catalyst.

Aldol-type condensation was then performed on the 4-heptanone product stream to further elongate the carbon chain to C_{14} and reduce the oxygen content. While significant work has been performed to date with terminal ketones,[21, 55, 56] condensation of internal ketones, such as 4-heptanone, is far less studied. Recently, Nb_2O_5 was identified as a highly selective catalyst (>80% carbon selectivity) to the dimer (mixture of positional and stereoisomers) for 4-heptanone condensation, but the chemistry has only been demonstrated for single-pass batch reactions with 8 wt% of 4-heptanone in toluene.[16, 21] When considering process design impacts, the relatively low ketone loading will require large equipment and high energy consumption for solvent separation. Therefore, we evaluated conversion efficiency at elevated ketone loadings with catalyst regeneration and recycle (Figure 6.4).

4-Heptanone condensation was performed in a bench-scale batch reactor. A commercial Nb_2O_5 catalyst acquired from CBMM was calcined at 350 °C prior to use, resulting in a surface area of 137 m^2 g^{-1} and total acidity of 255 µmol g^{-1} (Table E.2 in Appendix E). Initial
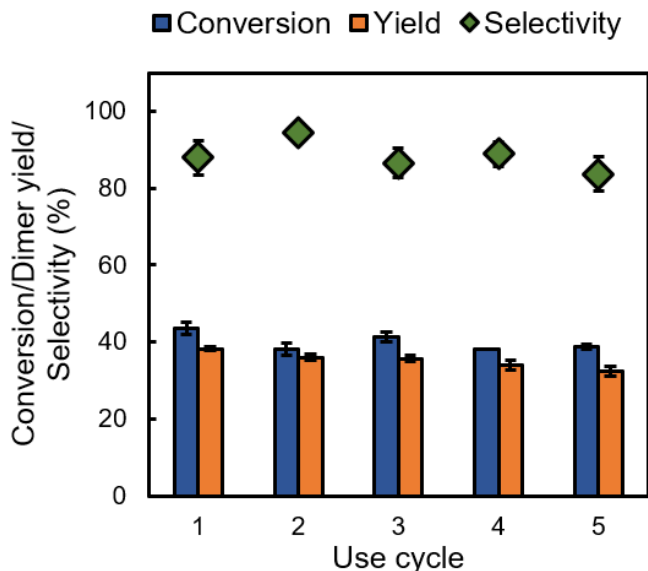
Figure 6.4 Nb$_2$O$_5$ reused for 4-heptanone condensation four times in a batch reactor by regeneration at 350 °C in between cycles. Reaction conditions: 15 g feed, 20 wt% 4-heptanone in toluene, 0.75 g catalyst, catalyst-to-ketone mass ratio = 1:4, initial He headspace at atmospheric pressure, 180 °C, 10 h.

experiments were performed using commercial 4-heptanone (98% purity, Sigma Aldrich) with a ketone loading of 20 wt% in toluene, ketone-to-catalyst mass ratio of 4:1, reaction temperature of 180 °C, and an initial atmospheric pressure He headspace. Under these conditions, conversion progressed rapidly in the first 3 h to 27% and then gradually to 58% after 24 h (Figure E.2a in Appendix E). At 24 h, selectivity to the desired dimer was 81%, similar to previous studies.[16, 21] The overall mass recovery was >98% with neglible mass loss to the gas phase, and the carbon mass recovery was >96%. The reactivity of 4-heptanone is significantly lower compared to that of the terminal ketone, as demonstrated for example by conversion of 2-heptanone reaching 90% in the first 3 h under similar conditions (data not shown). The lower reactivity is likely due to steric hindrance, making internal ketones inherently more difficult to process. The average reaction rate for 4-heptanone condensation plotted over time (Figure E.2b in Appendix E)

revealed rapid degradation in activity. A carbon content of 2.3 wt% was measured for spent Nb_2O_5 after 24 h reaction, suggesting fouling as a mode of deactivation.

To assess catalyst recyclability, spent Nb_2O_5 was washed with solvent, dried, and tested under the same reaction conditions as the fresh catalyst. Continuous decline in activity was still observed in subsequent reuses (Figure E.2c in Appendix E), likely due to incomplete removal of adsorbed species. Calcination of the spent catalyst in air at 350 °C for 12 h was then employed to regenerate the catalyst. Over four cycles of reuse, a 15% decrease in dimer carbon yield was observed (Figure 6.4). Surface area and total acidity of the regenerated catalysts showed insignificant change compared to those of the fresh catalyst, while small quantities of carbon residue were measured on the regenerated catalysts (Tbale E.3 in Appendix E). These observations suggest that the most active sites are vulnerable to deactivation and like not fully regenerated under mild conditions. Although carbon residue can be removed at higher calcination temperatures, further evaluation of catalyst activity will be needed as increasing temperature can lead to loss of water content and phase transition, accompanied by reduced surface area and acidity for this catalyst.[57]

Additional reaction conditions were then evaluated to further reduce solvent use and improve single-pass conversion by increasing the ketone loading (20 wt% to 100 wt.%), catalyst loading (catalyst-to-ketone mass ratio from 1:20 to 1:5), and operating temperature (180 °C to 220 °C). When the ketone loading increased from 20 wt.% to 100 wt.% (i.e., neat solvent-free) for a given catalyst loading, 10 h conversion decreased (Figure E.3a in Appendix E), while the average ketone reaction rate was nearly constant (Figure E.3b in Appendix E), indicating a high coverage of surface intermediates at these ketone loadings.[58] Increasing the catalyst loading under neat conditions increased dimer concentration in the liquid product (Figure E.3c in

Appendix E) but also enhanced carbon loss to catalyst surface. For example, 0.04 g carbon was measured for the spent catalyst at a catalyst-to-ketone mass ratio of 1:20, and this value increased more than three-fold to 0.13 g when the mass ratio increased to 1:5. With respect to operating temperature, raising the temperature from 180 °C to 220 °C at 20 wt.% ketone loading increased conversion by 30% after 10 hours of reaction but reduced dimer selectivity by 20% (Figure E.4a in Appendix E). Estimating the activation energy from Arrhenius plots was hindered Figure E.4b in Appendix E), potentially due to rapid carbon laydown from the reaction. Although beyond the scope of this study, high temperature processing of neat internal ketones requires further analysis to evaluate the tradeoff between increased conversion at the expense of selectivity and final fuel properties.

The final HDO step was then examined to convert the purified dimer into the target C_{14} hydrocarbon. The dimer feed was derived from commercial 4-heptanone and prepared by removing the reaction solvent and unreacted ketone through distillation, resulting in a mixture of 81% dimer and 19% non-target compounds. The latter may include higher boiling point trimer and larger oligomers that we were unable to identify by GC (Figure E.5 in Appendix E). HDO was performed in a packed bed flow reactor using a 3.3 wt% Pt/Al_2O_3 catalyst due to its metal-acid bifunctionality.[59, 60] The catalyst displayed a surface area of 198 m^2 g^{-1}, metal dispersion of 9.4%, and total acidity of 329 µmol g^{-1}, with the latter dominated by Lewis acidity (Table E.2 in Appendix E). At 334 °C and a WHSV of 4.4 h^{-1}, the dimer was completely converted with >97% overall mass recovery and >90% selectivity to a C_{14} hydrocarbon based on incoming dimer purity (Figure 6.5). Deoxygenation of the feed was also complete, resulting in a biphasic product comprising an organic phase (85 wt% C and 15 wt% H) and an aqueous phase. The C_{14} hydrocarbon was confirmed to exhibit the target structure by a combination of high-resolution

mass spectrometry (Figure E.6 in Appendix E) and nuclear magnetic resonance spectroscopy (Figure E.7 in Appendix E). A 10% decrease in C_{14} hydrocarbon yield was observed over 12 hours of time-on-stream due to an increasing degree of isomerization and cracking of the C_{14} hydrocarbon. The spent Pt/Al_2O_3 catalyst contained 5.5 wt% carbon, relatively small (<0.2%) compared with the total carbon mass processed. Regeneration by calcination completely restored the catalyst physicochemical properties (Table E.6 in Appendix E), indicating catalyst fouling as the likely cause for the decrease in C_{14} hydrocarbon yield. Future work is needed to identify the cause of catalyst fouling and understand its impact on reaction network and consequent change of product distribution.
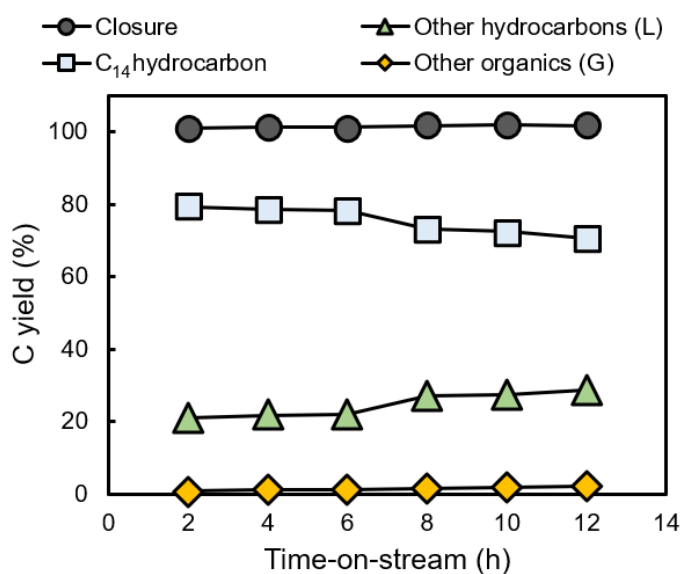
Figure 6.5 On-stream performance and product distribution of dimer HDO over 1 g Pt/Al_2O_3 in flowing H_2 [500 psi, 165 mL (STP) min^{-1}] at 334 °C and WHSV = 4.4 h^{-1}. The dimer feed (81% dimer purity) was derived from commercial 4-heptanone. WHSV was calculated using the mass flow rate of the dimer feed and the mass of the catalyst.

6.3.2.2 Integrated conversion of model and bio-butyric acid

Although the individual catalytic conversion steps above were demonstrated to have high selectivity (>85%) towards target products, the formation of non-target compounds poses additional challenges when using a fuel design approach based on evaluation of individual

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compounds. To this end, butyric acid was upgraded through the integrated catalytic conversion scheme shown in Figure 6.6. Starting with a model butyric acid feed, the ketonization resulted in complete butyric acid conversion with 13% carbon converted to CO_2 and 78% carbon converted to 4-heptanone (Figure 6.7). While the formation of CO_2 was stoichiometric and consistent with complete acid conversion, carbon yield to 4-heptanone was 88% of the theoretical yield. The remaining 9% of the carbon was retained in non-target byproducts primarily in the same phase as 4-heptanone. The organic phase of the liquid product was then decanted for separation from water. Note that carryover of water to the next conversion step may not affect process efficiency as the Nb_2O_5 catalyst used for ketone condensation is water tolerant.[24, 61]

The ketonization organic phase was then mixed with toluene at 20 wt% for the condensation reaction under the conditions shown in Figure E.2a in Appendix E. After 24 h, conversion of 4-heptanone reached 55% with an 82% selectivity to the dimer, nearly identical to the results obtained with commercial 4-heptanone (58% conversion and 81% selectivity). Due to byproduct formation during condensation, the fraction of carbon in the non-target compounds increased from 10% to 15% after the reaction (Figure 6.7). The reaction product was distilled to separate the dimer and heavier byproducts from solvent and ketone residue. Three fractions were obtained from distillation (Figure E.8 in Appendix E): solvent and unreacted ketone were primarily recovered in fractions 1 and 2, while fraction 3 comprised dimer (68% purity), heavier byproducts and minor lighter components (e.g., 2% 4-heptanone). Fraction 1 and 2 were recycled for condensation, and fraction 3 was used as the feed for the HDO reaction. Under the same operating conditions previously described (Figure 6.5), complete deoxygenation was achieved with selective conversion of dimer to the target C_{14} hydrocarbon at 65% purity in the organic phase (Figure 6.7). Organic phase non-target compounds included C_{14} hydrocarbon isomers,
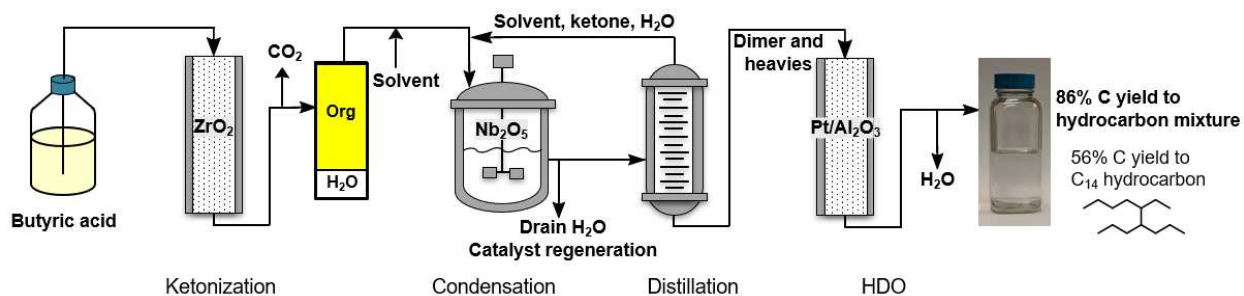
Figure 6.6 Integrated process scheme for upgrading butyric acid to hydrocarbon diesel blendstock.
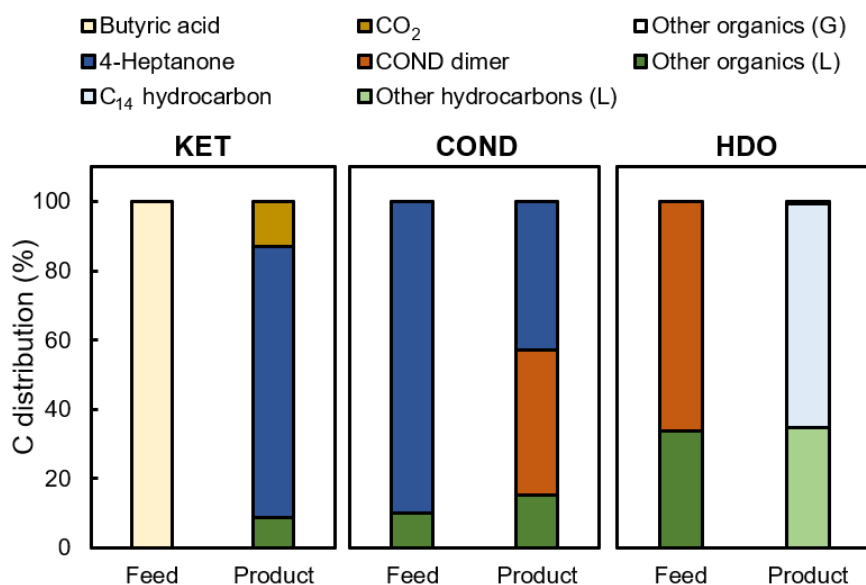
Figure 6.7 Carbon yield analysis of ketonization, condensation, and HDO when upgrading commercial butyric acid to hydrocarbon diesel blendstock through the integrated process scheme as shown in Figure 6.6. Conditions: ketonization same as in Figure 6.3; condensation same as in Figure E.2a in Appendix E, 24 h reaction, C distribution not accounting for solvent; HDO same as in Figure 6.5, 2 hours of time-on-stream. Analysis assumed ideal mass recovery.

other non-cyclic alkanes, cyclic alkanes, and a minor fraction of unsaturated structures (Figure E.9-E.11 in Appendix E). Assuming ideal separation and complete mass recovery during transfer,[25] the overall carbon yield of butyric acid to HDO organic phase was as high as 86%, while the overall carbon yield to the target C_{14} hydrocarbon was 56%. It is clear from these results that utilization of non-target hydrocarbons in the final diesel blendstock is critical to high carbon efficiency of the integrated process.

Finally, biologically-derived butyric acid was upgraded through the same integrated conversion scheme to demonstrate bioblendstock production from lignocellulosic biomass. Batch fermentation was performed with *Clostridium butyricum* on corn stover hydrolysate, the major components of which are glucose and xylose (Table E.5 in Appendix E).[62] Utilization of sugars in the hydrolysate was nearly complete after 56 h (Figure E.12a in Appendix E), and butyric acid was produced at a final titer of 20.4 g L^{-1} and yield of 0.32 g g_{sugar}^{-1} (Figure E.12b in Appendix E). A multi-step purification process recovered butyric acid from the fermentation broth at purity >99%, with separation optimization beyond the scope of this study.

Catalytic upgrading of the biologically-derived butyric acid achieved initial conversion efficiency and target product yield comparable to those from upgrading commercial butyric acid (Table 6.2). Under the same ketonization and condensation conditions, conversion of the target reactants and carbon yield to the desired products deviated by <2% from model compound experiments. After condensation, solvent and unreacted ketone were removed through distillation as previously described. Due to limited volume of the biologically-derived substrate, the feed for HDO was diluted with cyclohexane to facilitate sample handling. This modification did not change conversion efficiency, resulting in complete conversion of the dimer and production of an oxygen-free organic phase. The concentrations of non-metallic and metallic impurities in the biologically-derived feed and organic phase products were consistently low (Table E.6 in Appendix E, variation of Si may be due to the wear of reactor coating), suggesting an insignificant impact on catalyst performance or product purity for the time scale studied. However, the variety and level of impurities can vary greatly depending on biological conversion and separation conditions,[63-65] and a systematic evaluation of their impact on downstream catalytic processes is needed to provide valuable information for further process

integration with upstream processes. The target C_{14} hydrocarbon was produced at 61% purity in

the final hydrocarbon mixture product after solvent (cyclohexane) removal, comparable with the

results from upgrading commercial butyric acid. Carbon mass balance analysis was not

performed due to limited volume of biologically-derived materials. However, both similar

conversion performance (Table 6.2) and product gas chromatography profile (Figure 6.8)

suggest that the carbon efficiency of upgrading biologically-derived butyric acid can be

represented by those with commercial butyric acid, where the overall carbon yield to the final

hydrocarbon mixture product was 86%.

Table 6.2 Conversion of target reactants (butyric acid, 4-heptanone, and dimer) and carbon yield
to the desired products (4-heptanone, dimer, and C_{14} hydrocarbon, respectively) from upgrading
biologically-derived and commercial butyric acid through the integrated process scheme.

Conversion step	Bio-acid		Commercial acid	
	Conversion	Yield	Conversion	Yield
KET	100%	76%	100%	77%
COND	54%	42%	55%	45%
HDO	100%[a]	88%[a]	100%	87-97%

[a]Feed prepared by diluting distillation fraction 3 in cyclohexane at 20 wt.%, total feed WHSV = 8.2 h^{-1}.

6.3.3 Blendstock and blend fuel properties verification

Fuel properties were experimentally determined for both purified and crude C_{14}

hydrocarbon blendstocks to verify model predictions and evaluate fuel quality of the crude

conversion product mixture. Measured boiling point, LHV, flash point, and YSI of the purified

blendstock (94% purity, Table 6.3) were well within 10% of the predicted values summarized in

Table 6.1. Measured CN of an 81% C_{14} blendstock also matched the model prediction very well.

In contrast, the measured melting point was notably more than 40°C lower than the predicted

value. A melting point or cloud point below -80 °C indicates that this blendstock is likely

suitable for use in even the coldest environments. Predicted values for melting point deviated

substantially from experimental measurements. However, melting point prediction is inherently
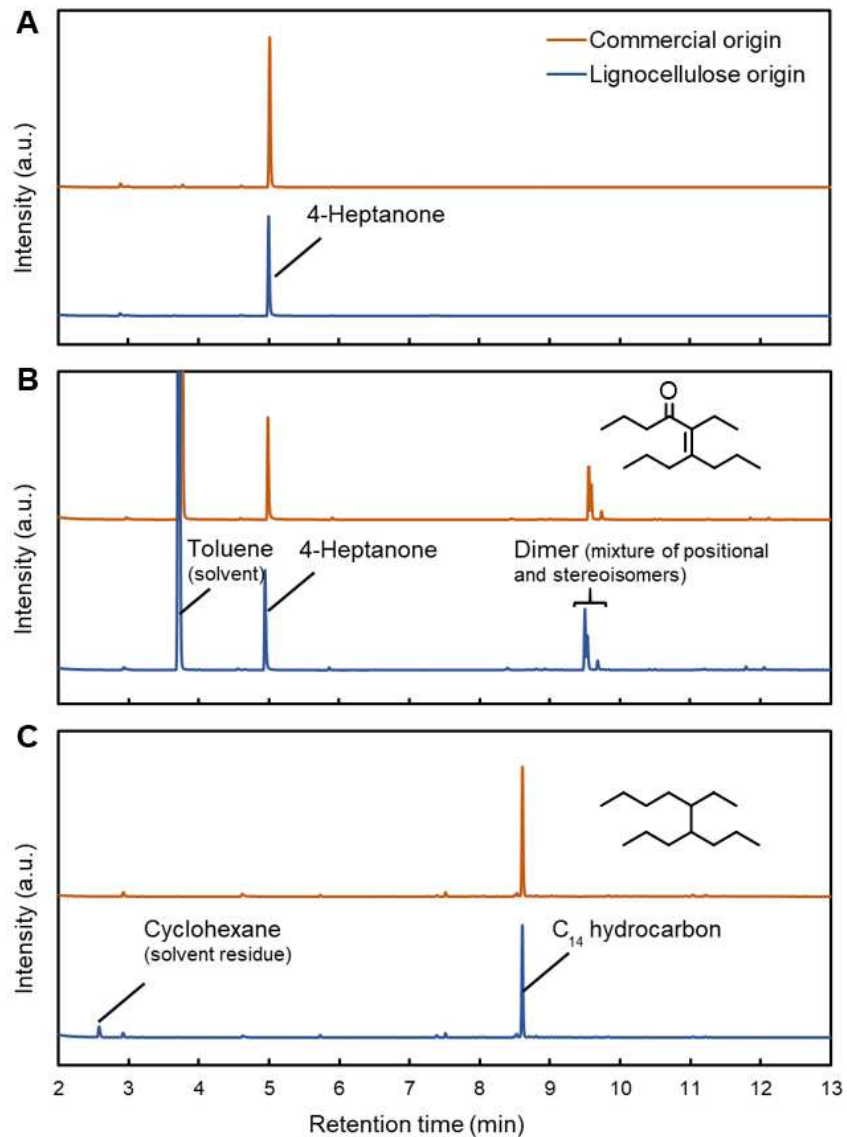
Figure 6.8 GC-Polyarc/FID chromatograms of organic phase products from (A) ketonization, (B) condensation, and (C) HDO (solvent was removed from biologically derived product by distillation) when upgrading butyric acid through the integrated process scheme.

difficult, with mean prediction errors often exceeding 40 °C.[66]

After verifying the target C_{14} molecule fuel properties, the crude blendstock was characterized to a similar extent to assess the impact of non-target compounds on fuel properties. Due to limited quantity of the biologically-derived materials, crude blendstock was prepared from commercial reagents. Compared with the purified blendstock, crude blendstock displayed

similar bulk properties, such as LHV and density (Table 6.3), which was expected given the target C_{14} hydrocarbon being the major component. In contrast to bulk properties, the crude blendstock exhibited a flash point 12 °C lower than that of the purified blendstock (Table 6.3). As previously shown, hydrocarbons with lower boiling point tend to have lower flash point (Figure E.1c in Appendix E). Therefore, the decrease in flash point was likely due to the short-chain hydrocarbons in the crude blendstock (<15 vol.% based on simulated distillation analysis), which resulted from HDO of 4-heptanone residue and undesired cracking reactions on acid catalysts. These low boiling point byproducts need to be monitored to ensure compliance with safety requirement. Nevertheless, the crude blendstock was well above the minimum flash point requirement for diesel fuels. To evaluate the sooting tendency of the crude blendstock on a volumetric basis that is consistent with volumetric blending, normalized soot concentration (NSC) was used. NSC is defined as the concentration of soot measured for a blendstock or a blend normalized to that of the base diesel (by definition having an NSC of 1). Both the purified and crude blendstocks exhibited NSC more than 50% lower than that of the base diesel, with the purified blendstock showing 21% lower NSC than the crude blendstock due to fewer non-target compounds (Table 6.3). Overall, these results validated the fuel properties of the crude blendstock and confirmed the successful conversion process development.

The promising fuel characteristics of the crude blendstock strongly indicate its suitability for use as drop-in diesel blendstock. This was further verified by measuring the fuel properties of a diesel blend containing a base diesel and 20 vol% crude blendstock derived from bio-butyric acid. The base diesel is a petroleum diesel (commercial additives were removed) that has excellent properties including low cloud point, high energy density, and cetane number. When comparing the measured fuel properties between the blend and the base diesel, it was evident that

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Table 6.3 Measured fuel properties of C_{14} blendstocks, base diesel, and a 20 vol% blend.

Properties	C_{14} blendstock		Diesel and blend	
	Purified	Crude[a]	Base diesel[b]	Blend[c]
Melting point (°C)	<-80	<-80	-9.7	-12
Cloud point (°C)	<-80	<-80	-7.6	-8.7
Boiling point (°C)	230	266[d]	333[d]	327[d]
Flash point (°C)	74	62[e]	55	54[e]
LHV (MJ kg^{-1})	44	44	45	43
LHV (MJ L^{-1})	34	34	39	37
CN[f]	ND	48[e]	47	46[e]
YSI	98	NA	NA	NA
NSC	0.37	0.47	1	0.89
Viscosity (cSt)	ND	1.49[e]	2.66	2.08[e]
Density (g mL^{-1})	0.78	0.78	0.86	0.85

ND = Not determined. NA = Not applicable. [a]Derived from commercial butyric acid (65% C_{14} purity). [b]Commercial additives were removed by clay treatment. [c]20 vol% bio-butyric acid derived blendstock (61% C_{14} purity) in base diesel. [d]T90 from simulated distillation profile. [e]20 vol% 4-heptanone derived blendstock (81% C_{14} purity). [f]Measured as indicated cetane number using ASTM method D8183.

the bioblendstock was able to maintain the base diesel quality (Table 6.3). For example, the bioblendstock slightly lowered the cloud point, demonstrating excellent solubility in the diesel fuel. The T90 was slightly reduced due to the lower boiling-range of the bioblendstock compared to the base diesel (Figure E.13 in Appendix E). Because the base diesel has a lower flash point than the blendstock, the flash point of the blend was dominated by that of the base diesel. The bioblendstock exhibited good ability to maintain diesel energy density compared with biodiesel and alcoholic diesel blendstocks,[67, 68] with only 5% reduction in blend LHV on either mass or volume basis. The measured CN of the blend was nearly unchanged and remained sufficiently beyond the minimum requirement of 40, which was expected considering the similar CN values between the base diesel and the blendstock (Figure E.14a in Appendix E). It is notable that the bioblendstock demonstrated the potential to reduce diesel soot formation, with the blend reducing NSC by 11% compared with the base diesel (Table 6.3). In addition, NSC appeared to linearly decrease with the blending volume of the bioblendstock (Figure E.14b in Appendix E), suggesting the potential to further reduce diesel sooting by increasing the blend ratio.

6.4   Discussion

To rationally target bioblendstocks that lead to advantageous properties, we leveraged fuel property prediction tools to inform the conversion pathway and molecule selection based on a "fuel property first" approach. This approach prioritizes fuel quality by estimating the fuel properties of potential products from an array of conversion pathways. We demonstrated this approach by employing a variety of empirical, predictive models derived from functional group contributions, molecular descriptors, and physical property correlations to screen 30 diesel-range hydrocarbon molecules accessible from short-chain C_2 and C_4 carboxylic acids derived from biological processes. This screening step allowed us to down-select butyric acid as the primary feedstock of interest for further catalytic upgrading to a non-cyclic branched C_{14} hydrocarbon as a potentially high combustion efficiency, low soot formation diesel blendstock. Tailoring hydrocarbon diesel blendstock from biological-chemocatalytic conversion routes is only one example of the "fuel property first" approach. This approach can be applied to diverse conversion routes and molecules accessible from lignocellulosic biomass[69-73] to accelerate biofuel development, and the growing availability of fuel property prediction tools and metrics[12, 52, 74-76] can also guide design for a variety of fuel applications and combustion modes.

Fuel property predictive models enable low-cost rapid fuel property evaluation by removing the sample quantity constraints associated with experimental synthesis and testing. This allowed us to evaluate six fuel properties related to handling and storage, fuel economy, and combustion performance, all of which are critical to successful fuel deployment. Notably, the YSI predictive model made it possible to screen fuel molecules for their sooting tendency, which is an emerging fuel property metric to evaluate particulate emissions.[47, 77, 78] Comparing fuel property predictions across an array of molecule candidates narrowed the candidate pool from 30

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down to 5 molecules; more importantly, it also provided quantitative information to facilitate further conversion pathway down-selection. Non-cyclic structures were identified as preferred targets for diesel applications, when compared to cyclic structures, due to the higher autoignition ability and lower sooting tendency of the former (Figure E.1e-f in Appendix E). Fuel property measurements of the target C_{14} hydrocarbon validated five out of six fuel property predictions, highlighting the value of the predictive models in rational fuel design.

Upgrading butyric acid through an integrated process scheme validated the conversion pathway and the advantageous fuel properties of the C_{14} hydrocarbon. Furthermore, conversion product analysis identified catalytic reaction byproducts as a key consideration for the "fuel property first" approach, which has rarely been addressed in fuel design. When producing the C_{14} hydrocarbon from butyric acid through sequential reactions, multiple non-target hydrocarbons were accumulated in the crude conversion product (Figures 6.7, Figure E.10 and E.11 in Appendix E) and entailed experimental evaluation of their influence on fuel properties. Although these non-target compounds did not significantly affect the bulk properties for the C_{14} blendstock, minor components have the potential to dramatically impact fuel properties at low levels, such as depressing flash point by >10°C with <15 vol.% low boiling point byproducts (Table 6.3). These observations encourage future consideration of conversion byproducts in the early phase of fuel design, which may be achieved by estimating the properties of mixtures for selected fuel parameters. A critical consideration for designing blendstocks is their blending behavior, and linear mixing rules have often been assumed to simplify prediction methodology in fuel blend design studies.[13, 79, 80] This simple blending behavior has been experimentally observed for bulk properties such as CN and viscosity with hydrocarbon mixture,[81, 82] whereas non-ideal behaviors are frequently reported for other properties and oxygenate-hydrocarbon mixtures.[68, 83-85] For our

bioblendstock blend, further testing is needed to determine the blend dependency since only single point blends measurements were performed. The ability to accurately predict mixture properties and blending relationships remains a grand challenge for computation and underscores the need to couple experimental validation of product fuel quality with the specific conversion routes and feedstocks of interest.

To further develop the butyric acid upgrading process we investigated, specific improvements can be made to each catalytic step. The initial acid ketonization reaction will likely not be a limiting step, as this work demonstrated complete butyric acid conversion and high molar selectivity (88%) to the target ketone under solvent-free and continuous production conditions and similarly high yields have been shown in other studies for acetic acid.[86, 87] Further improvement of selectivity may be attained by adjusting operating conditions and introducing metal sites to improve the reducibility of metal oxide catalysts.[88, 89] For 4-heptanone condensation, although we have demonstrated promising single-pass productivity at process-relevant ketone loadings, it will be important to understand the catalyst requirements and reaction mechanism for internal ketone condensation. Knowledge of both will be critical to developing effective strategies for increasing yields and stability,[90-93] as rapid catalyst deactivation has been reported with acid, base, and amphoteric catalysts for a broad class of aldol-type condensation reactions.[94-97] Introducing hydrogenation functionality to catalysts has shown promise to improve dimer selectivity or catalyst stability for C_3-C_6 methyl ketone or aldehydes,[55, 58, 97] but its potential to improve longer-chain internal ketone condensation still needs to be assessed. Lastly, continuous HDO was demonstrated with very high initial selectivity (98%) to the target hydrocarbon, but reversible catalyst deactivation by fouling resulted in gradual decrease in selectivity. To prevent catalyst fouling, further work is needed to identify if

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carbon deposition is caused by heavy compounds in the feed or *in situ* formation. Depending on the cause of deactivation, countermeasures can be taken such as pretreating the feed, tuning catalysts and process conditions, and controlling reaction rate regimes.[98, 99] When considering process integration, work is ongoing to improve the biological and separation efficiency of microbial acids, as well as understand the impact of biogenic impurities on catalyst performance.[62, 65, 100]

Lastly, based on promising fuel property validation results, the C_{14} blendstock warrants further engine testing to fully de-risk the bioblendstock from a fuel standpoint. Engine testing can assess fuel performance and quantify air pollutant emissions over a range of operating conditions reflective of use (e.g., compression ratio, air-fuel ratio, fuel injection pressure, cold starting).[101-103] Testing results can inform the "fuel property first" approach by improving our understanding of priority fuel property metrics that reflect desired engine and emission performance in actual use scenarios. Because traditional engine testing requires gallons of fuel, *in silico* and bench scale tools will be valuable to facilitating fuel performance evaluation. Bench scale evaluation of combustion kinetics can be performed with samples on the order of several hundred milliliters of bioblendstock,[104, 105] and these data can serve as the basis for kinetic simulations that could ultimately be used – in reduced form – as part of an engine simulation to predict efficiency and approximate emissions effects.[106, 107] Bench scale studies of fuel sprays and measurement of related properties can also inform these simulations.[108] Together with fuel property predictive models, these strategies can further accelerate the development of performance-advantaged bioblendstocks for diesel engines.

6.5   Conclusions

Advancement of renewable biofuels requires high quality bioblendstocks accessible from low-cost feedstocks with efficient conversion pathways. Here, we demonstrated a "fuel property first" design approach to access low-sooting, drop-in hydrocarbon diesel bioblendstock from lignocellulose derived short-chain carboxylic acids. By leveraging predictive models, critical fuel properties were rapidly screened for an array of hydrocarbons accessible from C_2/C_4 acids, leading to a down-selected conversion pathway targeting a non-cyclic branched C_{14} hydrocarbon molecule, 5-ethyl-4-propylnonane. Catalytic upgrading of butyric acid through an integrated process scheme showed high selectivity (>85%) for individual conversion steps and achieved >80% overall carbon yield to a hydrocarbon mixture product containing >60% of the target C_{14} hydrocarbon. The majority of fuel property predictions were verified using a purified C_{14} blendstock, while the crude conversion product exhibited similar bulk properties. Furthermore, blending of the C_{14} bioblendstock into a base diesel at 20 vol.% validated its suitability for use as a drop-in diesel blendstock, reducing soot formation of the base diesel by 10%. Overall, this work demonstrates the potential of a "fuel property first" design approach to inform conversion pathway development and produce advantageous bioblendstock from biomass.

6.6   Materials and Methods

6.6.1   Predictive models

Two models were used to estimate melting point. The first was sourced from commercial software, ChemDraw Professional 15.1 (PerkinElmer) which exploits both Joback's fragmentation method as well as Stein's modification to Joback's method.[33] The second prediction was obtained from the estimation program MPBPWIN™ in EPI Suite™ (US EPA, Syracuse Research Corp.).[34] This program estimates melting point by giving a weighted average

of the results of two methods, the Joback Method (a group contribution method) and the Gold and Ogle method (a correlation between melting point and boiling point). Boiling point predictions also utilized the ChemDraw and EPI Suite tools, with the addition of a third available predictive model developed by Satou et al.[36] Flashpoint was estimated via two predictive models, both requiring a reliable boiling point. One of the earliest was developed by Butler *et al.*,[37] which was built on correlation for petroleum boiling in the range of about 90 to 370 °C. The second correlation was later developed by Prugh and based on a larger database of hydrocarbons and fuel mixtures.[38] Numerous predictive models for the higher heating value for a variety of samples have been developed, primarily based around species mass contributions. The first model applied in this work is the Dulong equation, which was used to determine higher heating value estimates for coal and fossil fuels.[42] This work also includes two predictive estimates which are from modifications to Dulong's formula. Lloyd and Davenport[43] included ethers and other oxygenates in their modification, and Boie[44] adapted the formula for a larger dataset. Lower heating values reported here are determined by the following equation, which is a function of the estimated mass% hydrogen (H) in a sample (ASTM D240, Section 10.5.1).[109]

$$LHV = HHV - (0.2122*H) \tag{6.1}$$

Cetane number predictions were produced using a back-propagating artificial neural network (ANN) with inputs including experimental CN values and quantitative structure-property relationships (QSPR) for individual molecules. The model uses an iterative regression analysis technique to reduce the number of input parameters; in the case of CN, from >1500 to 15. The ANN randomly assigns an individual molecule from the known data set to one of three conditions: learning, validation, and testing, with proportions of 65%, 25%, and 10% respectively. The trained model is subsequently applied to the new molecule of interest's QSPR

parameters in order to produce a predicted CN. The method has been shown to provide high accuracy and repeatability across a broad range of hydrocarbons when predicting CN.[45, 46] Yield sooting index predictions were generated using a group contribution model that sums contributions from each carbon atom.[47]

6.6.2 Catalytic upgrading

Commercial butyric acid, 4-heptanone, toluene and cyclohexane were purchased from standard chemical suppliers such as Sigma-Aldrich or Acros. Biologically derived butyric acid was obtained from lignocellulosic sugars fermentation as detailed in Appendix E.

Fresh catalysts and selected post-reaction catalysts were characterized by N_2 physisorption, ammonia TPD, pyridine DRIFTS, chemisorption, and TGA-IR. Details on catalyst synthesis and characterization methods are provided in Appendix E.

Packed-bed reactor experiments were performed in a stainless-steel tubular reactor system. The reactor tube was coated with a silica Dursan coating provided by SilcoTek Coating Co. Batch reactor experiments were performed in a Parr multi-batch reactor system (Parr Instrument Co.), and the reactors were also coated with the silica Dursan coating. Liquid products were analyzed by gas chromatography with a flame ionization detector and a mass spectrometer (GC-FID/MS). Carbon, hydrocarbon, nitrogen, sulfur, and metals analyses were performed by Huffman Hazen Laboratories. Selected samples were analyzed by high resolution mass spectrometry, nuclear magnetic resonance spectroscopy, and two-dimensional gas chromatography with time-of-flight mass spectrometry (GC×GC-TOFMS). Further details on catalytic testing systems, data analysis, and analytical methods were provided in Appendix E.

6.6.3   Fuel property testing

Cetane number was measured as indicated cetane number using 40 mL of sample in an AFIDA instrument (ASTM D8183). Boiling point was estimated using simulated distillation (D2887). Higher heating value was measured by combusting samples in a bomb calorimeter (D240), with hydrogen content used to calculate lower heating value being measured for each sample using a LECO TruSpec CHN determinator. Samples were combusted at 950 °C under a flow of excess oxygen and the gas produced was analyzed with infrared spectroscopy to quantify the amount of CO_2 and H_2O produced. Ethylenediaminetetraacetic acid (EDTA) was used as the calibration standard. Density was found using a Mettler-Toledo DM40 density meter (D4052). Viscosity was measured at 40 °C using D445 or a TA Instrument AR1500 equipped with a recessed rotor at a shear rate of 1-100 s^{-1}. Melting point and cloud point was measured using a Phase Technology Series 70X (a modified version of D5773). Flash point was measured using D7094. Two different types of sooting tendency measurements were performed. Measurement of YSI followed published procedures.[110] Briefly, samples of the test substance, n-heptane, and toluene were doped into the fuel of a methane/air nonpremixed flame at a mole fraction of 1000 ppm. Soot concentrations in the resulting flames were quantified with line-of-sight spectral radiance (LSSR). The maximum LSSR in each flame was then converted to a YSI by a linear rescaling with the specified endpoints of n-heptane = 36.0 YSI units and toluene = 170.9 YSI units. To obtain normalized soot concentration (NSC), the same procedures were followed except that all of the dopants were added at a fixed volumetric flowrate of 100 μL h^{-1}. The results were not indexed to toluene and heptane; instead the soot concentration from the undoped flame was subtracted off and then the concentration attributable to the dopant was normalized to the value for the reference base diesel fuel.

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CHAPTER 7

SUMMARY, CONCLUSIONS, AND FUTURE WORK

7.7   Conclusions

This work identified alternatives to Pd-based catalysts for catalytic reduction of water pollutants and integrated catalysts with other processes to advance the application of catalytic reduction for drinking water treatment. The major findings are summarized as below.

Supported catalysts of four platinum group metals (Ru, Rh, Ir, and Pt) were shown to exhibit favorable reactivity with aqueous bromate, chlorate, nitrate and perchlorate at ambient conditions. Specifically, Rh and Ru showed significant advantages over Pd in terms of catalytic turnover frequency, pH dependence, oxyanion substrate scope, or cost. Cross comparison of multiple metals and tri-oxyanion substrates suggested that some previous interpretations of the pH influence on catalyst reactivity should be revisited. The chemical nature of each metal element is a key factor determining the catalyst activity and adaptability to different water treatment conditions.

It was then demonstrated that supported Ru catalysts, which are much lower in cost than Pd-based catalysts, have a high intrinsic activity in nitrate activation. The key features for supported Ru catalysts that need to be controlled to achieve high activity are that reduced Ru surface can be obtained by H_2 reduction at reaction temperature and that the surface is not blocked by residues from the synthesis process or other surface-active substrates. Ru reduced nitrate selectively to ammonia, while nitrite was reduced to a mixture of N_2 and ammonia, with selectivity shifting towards N_2 at increasing nitrite:hydrogen ratio. The reaction mechanism was proposed that sequential hydrogenation of nitrate to nitrite and NO is followed by parallel

pathways involving the adsorbed NO: (1) sequential hydrogenation to ammonia, and (2) N-N coupling with aqueous nitrite followed by hydrogenation to the detected N_2O intermediate and N_2 endproduct.

Supported Ru catalysts were further shown to rapidly reduce *N*-nitrosodimethylamine (NDMA), a highly toxic nitrogenous disinfection byproduct that poses significant challenges to potable water reuse systems. The high activity was demonstrated with both commercial and in-house prepared Ru/Al_2O_3 catalysts, with the commercial material yielding an initial metal weight-normalized pseudo-first-order rate constant (k_0) of 1103 ± 133 $L \cdot g_{Ru}^{-1} \cdot h^{-1}$ and an initial turnover frequency (TOF_0) of 58.0 ± 7.0 h^{-1}. NDMA was reduced to dimethylamine (DMA) and ammonia end-products, and a small amount of 1,1-dimethylhydrazine (UDMH) was detected as a transient intermediate. Experiment with a mixture of five *N*-nitrosamines spiked into tap water (1 µg L^{-1} each) demonstrated that Ru catalysts are very effective in reducing a range of *N*-nitrosamine structures at environmentally relevant concentrations.

Based on these promising results with Ru catalysts, this work demonstrated a hybrid catalytic hydrogenation/membrane distillation process to enable nitrate-contaminated ion exchange brine reuse and capture nitrogen as potential fertilizer product. A commercial Ru/C catalyst was able to hydrogenate nitrate in typical waste brine conditions including conditions representative of expected considering salt buildup upon brine reuse without requiring solution pH control. In a real ion exchange waste brine, nitrate was hydrogenated to ammonia at high selectivity. The resulting ammonia product was efficiently recovered using membrane distillation. The ammonia mass transfer efficiency was favored by high solution pH and temperature and not affected by salt concentration.

Overall, this work revealed the importance and feasibility of applying metal catalysts alternative to Pd-based materials for catalytic water treatment. Particularly, supported Ru catalysts demonstrated cost competitiveness and high catalytic activities with a range of contaminants, encouraging further catalyst development and process integration to advance the development of practical water catalysis technologies.

In the last part of this dissertation, a "fuel property first" design approach was demonstrated to access low-sooting, drop-in hydrocarbon diesel bioblendstock from lignocellulose derived short-chain carboxylic acids. By leveraging predictive models, critical fuel properties were rapidly screened for an array of hydrocarbons accessible from C_2/C_4 acids, leading to a down-selected conversion pathway targeting a non-cyclic branched C_{14} hydrocarbon molecule, 5-ethyl-4-propylnonane. Catalytic upgrading of butyric acid through an integrated process scheme showed high selectivity (>85%) for individual conversion steps and achieved >80% overall carbon yield to a hydrocarbon mixture product containing >60% of the target C_{14} hydrocarbon. The majority of fuel property predictions were verified using a purified C_{14} blendstock, while the crude conversion product exhibited similar bulk properties. Furthermore, blending of the C_{14} bioblendstock into a base diesel at 20 vol% validated its suitability for use as a drop-in diesel blendstock, reducing soot formation of the base diesel by 10%. Overall, the potential of the "fuel property first" design approach to inform conversion pathway development and produce advantageous bioblendstock from biomass was demonstrated.

7.7 Future Work

Results in chapter 2 identified that catalytic activity of supported metal catalysts for hydrogenating individual substrate primarily depends on the chemical nature of the metal. Further work is needed to provide greater mechanistic insights into these relationships, which is

important to rational catalyst design and informs catalytic water treatment process design. A common approach to investigating activity trend is to plot the measured activity over chemical descriptors such as the adsorption energy of reactants (e.g., hydrogen) or reaction intermediates (e.g., NO during nitrate and nitrite reduction) on metal surface. This type of plot often leads to unambiguous identification of the optimal binding energy and the type of metal imparting such properties. Even though it does not require detailed reaction pathway study to perform such analysis, the most relevant chemical descriptors are likely those involved in the rate-limiting step. Identification of the rate-limiting step can be achieved by experimental approach (e.g., kinetic analysis, isotope exchange test), Density Functional Theory calculation, or a combination of both.

Chapter 3 provided a more in-depth investigation of nitrate and nitrite hydrogenation with supported Ru catalysts, including reaction kinetics, pathway, and the influence of catalyst pretreatment on activities. This work identified factors that have significant impact on catalyst activity and product selectivity, which suggest a target for future Ru catalyst design. For example, surface alloying may be used to improve catalyst activity at higher nitrate concentrations by reducing the binding strength of nitrite, or to open up alternative N–N coupling pathway by altering the surface species diffusion rates.

Both chapter 3 and chapter 4 showed that catalyst performance depends on the size and morphology of the metal nanoparticles for supported metal catalysts. The catalyst structure-activity relationship was not explored in detail in this work, but this is an important area to study in future work to inform catalyst development. To study the influence of catalyst structure or surface properties on catalyst activity, a series of supported metal catalysts can be synthesized with various metal loading or using different synthetic techniques, followed by extensive characterization of structural and chemical properties. By comparing catalytic activity among

these catalysts, the critical structural or chemical properties may be identified. Alternatively, synthetic control strategies can be leveraged to obtain catalysts with uniform nanoparticle size and shape, facilitating the elucidation of surface site distribution (e.g., different facets, terrace versus edge sites) to catalyst activity. The potential interaction between catalyst support and metal nanoparticle needs to be considered during experimental design as well.

The ability of Ru/C for efficient nitrate hydrogenation was demonstrated in a semi-batch reactor under both freshwater conditions (chapter 3) and ion exchange waste brine conditions (chapter 5). Moving towards practical application, efforts are required to develop and evaluate other reactor configurations. Particularly, packed-bed reactors have the advantage of easy liquid-catalyst separation and low catalyst attrition rate, resulting in their wide adoption in petroleum processing and chemical production. Supported Ru catalysts in pellet or extrude form need to be synthesized using scalable synthesis method and evaluated for catalyst activity under various packed-bed reactor operating conditions. Catalyst performance will likely depend on H_2 mass transfer rate, solution chemistry and temperature. When treating concentrated nitrate in ion exchange waste brine, H_2 mass transfer can become a major limitation. Increasing H_2 pressure warrants further study as it is expected to improve H_2 gas-liquid transfer rate and enhance surface kinetics for nitrate hydrogenation. Alternative H_2 source (e.g., formic acid) and delivery mechanism (e.g., electrochemical system) are worth exploring with Ru catalysts as well. Continuous treatment of realistic matrices needs to be demonstrated at more industrially-relevant timescale to assess catalyst stability and identify the potential deactivation mechanism. Subsequently, catalyst regeneration and source water pretreatment strategies need to be studied to extend catalyst lifetime. Finally, there are tremendous opportunities for further techno-economic analysis and life cycle assessment of Ru catalyst systems to identify performance and

lifetime benchmarks and evaluate their potential advantage over Pd catalysts and existing technologies.
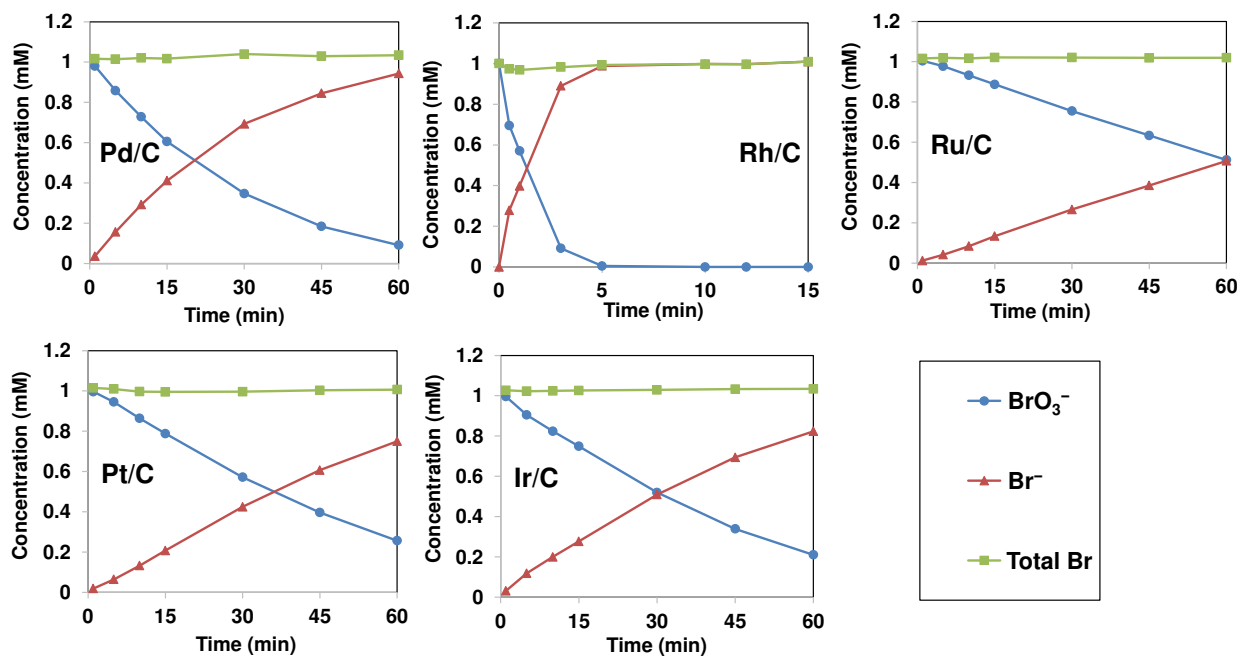
Figure A.1 Timecourse profiles with Br mass balance for reduction of 1 mM BrO_3^- and Br^- product formation using 0.1 g L^{-1} M/C (nominal 5 wt% metal for Pd, Rh, Ru, and Pt; 1 wt% metal for Ir) and 1 atm H_2 (100 mL min^{-1} sparging rate) at pH 7.2, 22 °C.
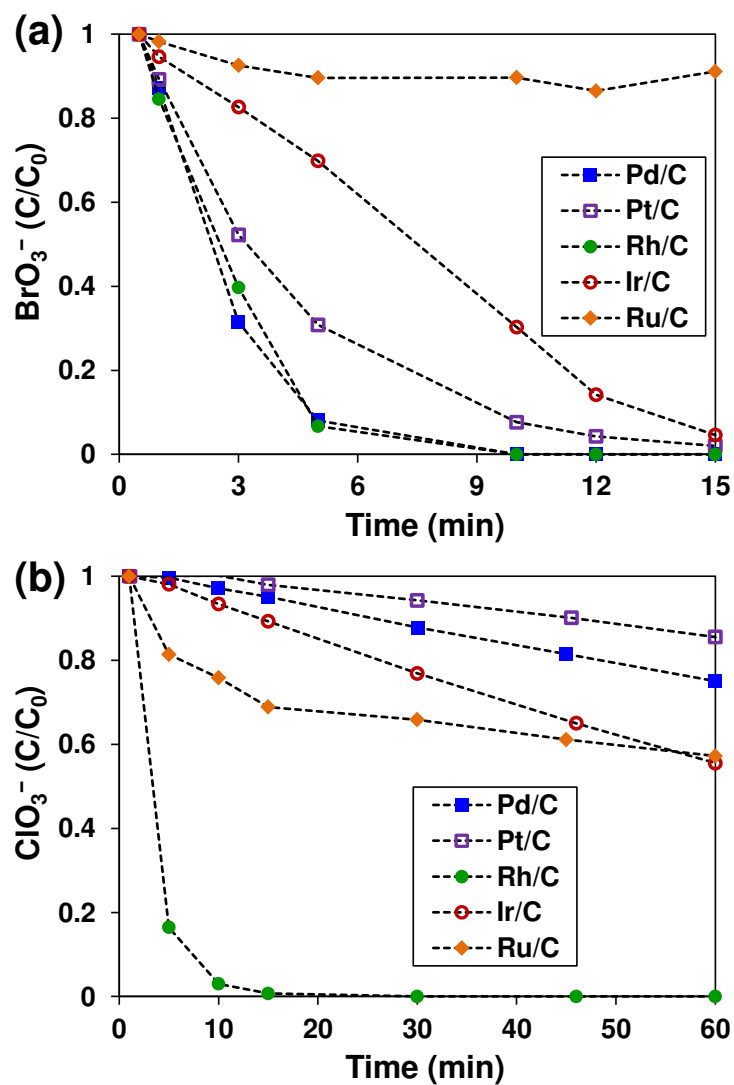
Figure A.2 Timecourse profiles observed at acidic pH conditions (pH 3.0) for reduction of (a) 1 mM BrO_3^- by 0.1 g L^{-1} M/C catalysts and (b) 1 mM ClO_3^- by 0.5 g L^{-1} M/C catalysts. All experiments were carried out in continuously mixed aqueous suspensions and sparged with 1 atm H_2 at 22 °C.

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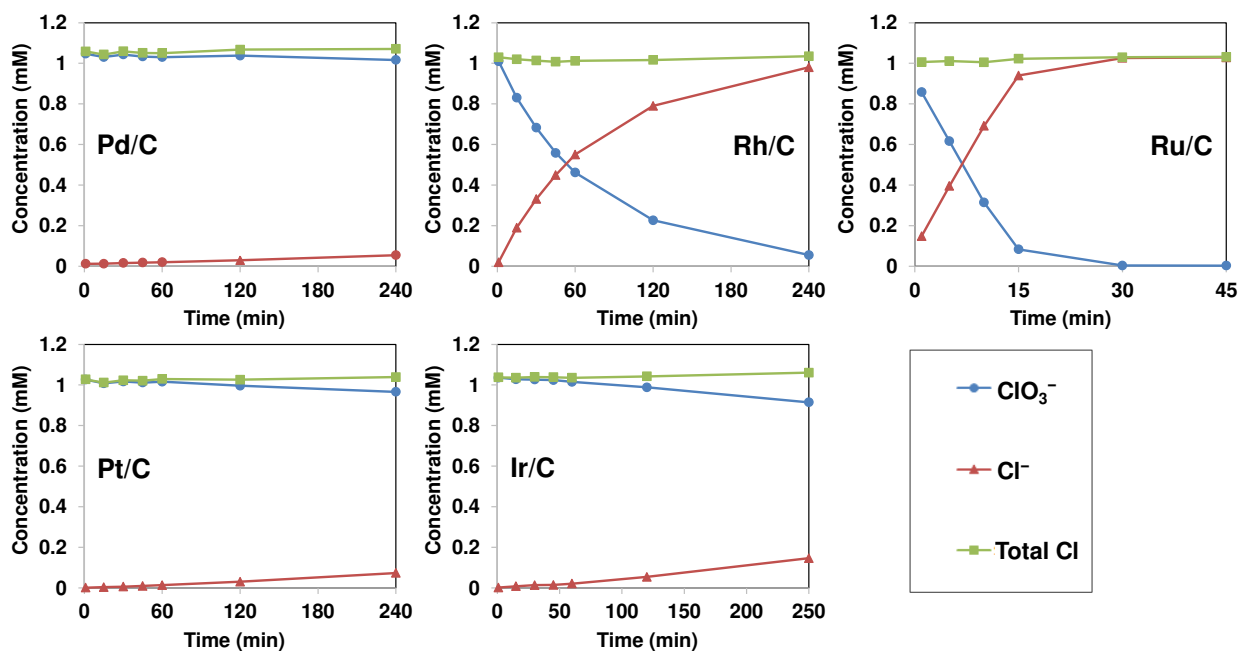
Figure A.3 Timecourse profiles with Cl mass balance for reduction of 1 mM ClO_3^- and Cl^- product formation using 0.5 g L^{-1} M/C (nominal 5 wt% metal for Pd, Rh, Ru, and Pt; 1 wt% metal for Ir) and 1 atm H_2 (20 mL min^{-1} sparging rate) at pH 7.2, 22 °C.
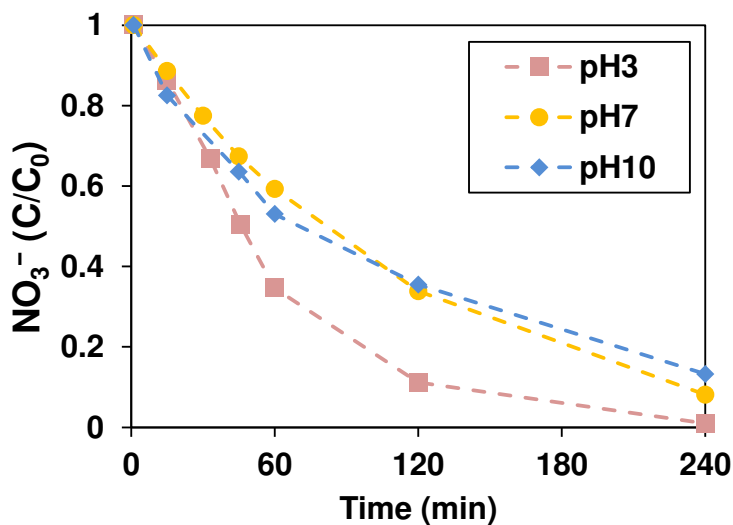
Figure A.4 Reduction profiles for 1 mM NO_3^- by 0.5 g L^{-1} Ru/C catalyst at different pH.

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Table A.1 Market price range of the five hydrogenation metals.[a]

	6-month price range (US $ per gram)	5-year price range (US $ per gram)
Pd	17~23	16~29
Rh	20~24	20~80
Ru	1.35	1.3~5.8
Pt	30~38	27~61
Ir	17~21	13~35

[a]Data collected from http://www.infomine.com as of September 2016.

Table A.2 Perchlorate reduction results by M/C catalysts (without Re).[a]

	Reaction time	pH	C/C_0
Pd/C	8 h	3.0	1.02
Rh/C	8 h	3.0	0.99
Ru/C	25 h	3.0	1.01
Ru/C	25 h	7.2	1.03
Pt/C	8 h	3.0	0.99
Ir/C	8 h	3.0	1.01

[a]Reaction conditions: ClO_4^- C_0 = 1 mM, 2.0 g L^{-1} catalyst, 1 atm H_2, 22 °C.

APPENDIX B

SUPPLEMENTARY DATA FOR CHAPTER 3

B.1 Experimental Methods

B.1.1 Chemical reagents

Ru on carbon (Ru/C, catalog # 206180), Ru on alumina (Ru/Al$_2$O$_3$, catalog # 381152), Pd on carbon (Pd/C, catalog # 330116, dried in the air) and Pd on alumina (Pd/Al$_2$O$_3$ catalog # 205710), all in the form of a nominal 5 wt% noble metal, were purchased from Sigma-Aldrich. NaNO$_3$ (≥99.0%), Na^{15}NO$_3$ (98 atom % ^{15}N), ^{15}N$_2$(g) (98 atom % ^{15}N), Cu(NO$_3$)$_2$·3H$_2$O (puriss. p.a., 99-104%), In(NO$_3$)$_3$·3H$_2$O (99.999%) and MES hydrate pH buffer (≥99.5%) were also obtained from Sigma-Aldrich. Reagent-grade HCl and NaOH were purchased from Fisher Scientific. Na^{15}NO$_2$ (≥98%) was obtained from Cambridge Isotope Laboratories. Cylinders of ultrahigh purity H$_2$(g) (99.999%) and N$_2$(g) (99.999%) were supplied by Matheson Tri-Gas. Deionized water (≥18 MΩ cm^{-1}; Barnstead Nanopure system) was used for all experiments.

B.1.2 Catalyst characterization

Metal contents were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) (PerkinElmer Optima 2000DV) after digestion in HNO$_3$-H$_2$O$_2$ (for Pd catalysts) or KOH-KNO$_3$ (for Ru catalysts). Specific surface area, total pore volume, and average pore diameter of the support materials were determined by N$_2$ physisorption after degassing at 350 °C for 2 h (Micromeritics ASAP 2020 analyzer); the BET method was used to calculate specific surface area.

Metal dispersion, defined as the percentage of Ru or Pd atoms present on the clean surface of the immobilized metal nanoparticles, was estimated by CO chemisorption using a Micromeritics AutoChem II analyzer equipped with a thermal conductivity detector (TCD). Clean metallic surface was obtained by reducing the as-received catalysts at 350 °C in flowing H_2 (10 mL min^{-1}) for 2 h followed by cooling the material to 25 °C in flowing He. The CO chemisorption was conducted in a pulse manner. The temperature of the sample was maintained at 25 °C. A small dose of CO was repeatedly supplied to the catalyst. CO chemically reacts with metal active sites until all actives sites have reacted. The quantity of CO molecules chemisorbed is the difference between the total amount of CO gas supplied and the sum amount that did not react with the catalyst as measured by the detector. Metal dispersion was calculated following the equation below.

$$\text{Metal dispersion (\%)} = \frac{\text{CO uptake}}{\text{CO:Metal ratio}} \times \frac{M}{W_{\text{metal}}} \times 10^{-6} \left(\frac{\text{mol}}{\mu\text{mol}}\right) \times 100 \qquad \text{(B.1)}$$

where CO uptake is the quantity of CO molecules chemisorbed on the catalyst (μmol g_{cat}^{-1}), M is the active metal's atomic weight (g mol^{-1}), and W_{metal} is the metal wt fraction of the catalyst. A CO:Metal (Ru or Pd) stoichiometric ratio of 1:1 was assumed.[1, 2]

Active surface, defined as the percentage of Ru or Pd atoms accessible to reactants under simulated *in situ* conditions, was measured by using a CO chemisorption protocol adapted to simulate the *in situ* reduction of catalyst surfaces that occur in the semi-batch reactor where oxyanion reaction kinetics were determined. Prior to CO pulse delivery, catalysts were reduced at 25 °C in flowing H_2 (10 mL min^{-1}) for 30 min, followed by purging with He to remove weakly physisorbed H_2. Active surface was calculated using the same equation as metal dispersion except that the value of CO uptake was obtained from a different protocol.

Morphology of the supported metal nanoparticles was characterized by high angle annular dark field (HAADF) imaging with scanning transmission electron microscopy (FEI Titan S/TEM operated at 200 kV) or bright field imaging with transmission electron microscopy (TEM; Philips/FEI CM200 microscope operated at 200 kV). Samples were dispersed in methanol and mounted onto holey carbon Cu grids prior to analysis. To obtain the particle size distribution, at least 150 particles were counted for each image. Long-range structural order was determined by powder X-ray powder diffraction (XRD; Siemens, Kristalloflex 810, Cu Kα radiation). The X-ray source was set 30 kV and 25 mA, with a sampling step of 0.02° and dwell time of 1 s. Spectra were compared to reference card files from the International Center for Diffraction Data (ICDD) database. Ru reducibility was determined by H_2 temperature-programmed reduction (TPR) using the same instrument used for CO chemisorption analysis. Samples were first treated with flowing Ar at 20 °C for 60 min to remove any air trapped in the catalysts prior to being heated to 800 °C at 10 °C min^{-1} in a gas stream of 10% H_2/Ar.

B.1.3 Calculation of kinetic parameters

Catalyst activity was assessed by measuring initial mass-normalized pseudo-first-order rate constants (k_0, L $g_{Ru/Pd}^{-1}$ min^{-1}) and turnover frequencies (TOF$_0$, min^{-1}), defined as the number of nitrate or nitrite ions reduced per active catalyst surface site per minute. Initial observed pseudo-first-order rate constants ($k_{obs,0}$, min^{-1}) were determined by fitting the natural log of NO_3^- or NO_2^- concentration versus time data for the first reaction half-life, and the corresponding mass-normalized rate constants were determined by:

$$k_0 = \frac{k_{obs,0}}{C_{catalyst}W_{metal}} \qquad (B.2)$$

where $C_{catalyst}$ is the catalyst mass loading in the aqueous suspension (g L^{-1}). The corresponding TOF_0 value was then calculated by dividing the product of the $k_{obs,0}$ and the initial oxyanion concentration (C_0, mol L^{-1}) by the concentration of active surface Ru or Pd atoms ($C_{metal\ surface}$, mol L^{-1})[3]:

$$TOF_0 = \frac{k_{obs,0}C_0}{C_{metal\ surface}} = \frac{k_{obs,0}C_0M}{\text{Active surface} \times C_{catalyst}W_{metal}} \tag{B.3}$$

where $C_{metal\ surface}$ is estimated from active surface coupled with information on $C_{catalyst}$, W_{metal} and M.

B.1.4 Analytical methods

Aqueous nitrate and nitrite concentrations were analyzed by ion chromatography with conductivity detection (Dionex ICS-2100 system; Dionex IonPac AS19 column; 20 mM KOH as eluent; 1 mL min^{-1} eluent flow rate). Total ammonia (NH$_3$/NH$_4^+$) was analyzed by colorimetric analysis (Hach salicylate method). Headspace samples in closed batch reactor experiments were analyzed for ^{15}N-labeled products by gas chromatography with mass spectrometry (GC-MS; Agilent Technologies; 6850 Network GC System; 5975C VL MSD with Triple-Axis Detector; Column, Varian Plot CP-Molsieve 5Å, 25 m × 0.25 mm; oven temperature 165 °C; He carrier gas, 1.0 mL min^{-1}). ^{15}N$_2$ calibration standards were prepared by adding known masses of ^{15}N$_2$ to 160 mL serum bottles containing 75 mL DI water and 85 mL headspace filled with H$_2$ (the same water and headspace volumes as the catalyst-containing closed reactors). Six standards, ranging from 2.05 µmol to 40.9 µmol ^{15}N$_2$-N, were prepared. After equilibrating the labeled standard in the reactor, 0.1 mL of headspace was collected by gas tight syringe and injected onto the GC-MS. As the total amount of ^{15}N$_2$ in the reactor (including headspace and aqueous phase) is linearly proportional to ^{15}N$_2$ concentration in the headspace, the calibration curve for total ^{15}N$_2$

was developed by plotting the peak area of the selected species (m/z = 30 for $^{15}N_2$) against the total moles of N as $^{15}N_2$ added to the reference standard reactor (Figure B.1 in Appendix B).
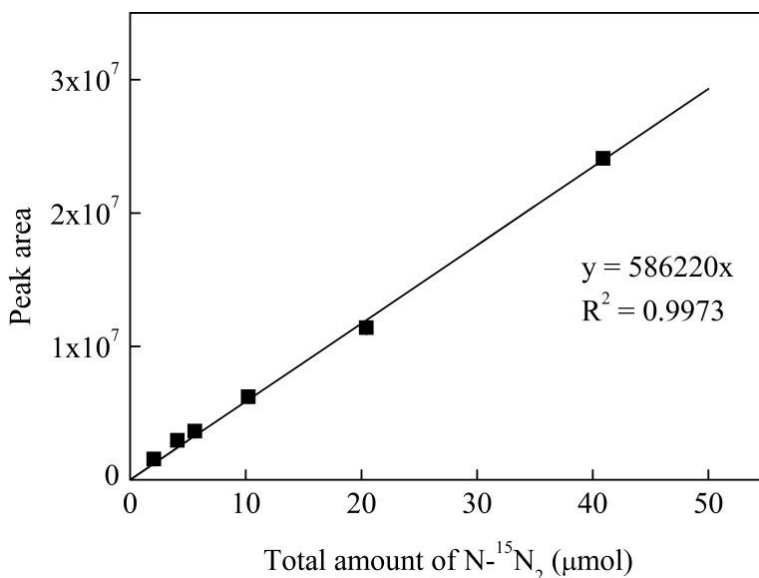
Figure B.1 Example calibration curve of total N-$^{15}N_2$ in the reactor.

In the absence of a $^{15}N_2O$ standard, a relative response factor (RRF) between N_2 and N_2O determined in a previous study that used the same instrument and analytical method[4] was used to estimate $^{15}N_2O$ quantities in this study assuming that the RRF between N_2 and N_2O is the same as the RRF between $^{15}N_2$ and $^{15}N_2O$:

$$RRF = RF_{N_2O}/RF_{N_2} = RF_{15N_2O}/RF_{15N_2} \tag{B.4}$$

where RF refers to a response factor, which is the ratio between the concentration of a compound and the response of the mass spec detector to the compound. The RFs for the gas species were calculated by dividing the peak area integrated from the chromatogram of selected species by the concentration of the species in the headspace gas sample:

$$RF_{N_2} = \frac{\text{Peak area}}{C_{N_2, g}} \tag{B.5}$$

$$RF_{N_2O} = \frac{\text{Peak area}}{C_{N_2O, g}} \tag{B.6}$$

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The calibration curve for $^{15}N_2O$, which is the relationship between the integrated peak area of $^{15}N_2O$ and the total amount of $^{15}N_2O$ in the reactor, can be obtained from the following equation:

$$\text{Total } 15N_2O = \left(K_{H,N_2O}RTV_a + V_g\right) \times C_{15N_2O,\, g}$$

$$= \left(K_{H,N_2O}RTV_a + V_g\right) \times \frac{\text{Peak area}_{15N_2O}}{RRF \times RF_{15N_2}}$$

$$= \frac{\left(K_{H,N_2O}RTV_a + V_g\right) \times \text{Peak area}_{15N_2O} \times \text{Total } 15N_2}{RRF \times \left(K_{H,N_2}RTV_a + V_g\right) \times \text{Peak area}_{15N_2}} \tag{B.7}$$

The Henry's constant values for N_2O and N_2, $K_{H,\,N2O}$ and $K_{H,\,N2}$, are 2.4×10^{-2} M atm^{-1} and 6.5×10^{-4} M atm^{-1}, respectively,[5] V_a is the volume of the aqueous phase (75 mL), V_g is the volume of the headspace (85 mL), R is the gas constant (0.082 L atm K^{-1} mol^{-1}), T is absolute temperature (294.15 K), RRF is calculated to be 3.16 based on the slopes of the calibration curves of N_2 and N_2O,[4] and the ratio between the peak area of $^{15}N_2$ and total amount of $^{15}N_2$ can be obtained from Figure B.1 in Appendix B.

B.2   Experimental Results

B.2.1   Evaluation of mass transfer limitation

Data presented in Figure B.2 in Appendix B support the conclusion that reaction is not limited by external mass transfer processes at the conditions used in experiments. The Weisz-Prater parameter (C_{WP})[6] provides a measure of the characteristic time scale of an observed reaction in comparison to the estimated characteristic time for internal diffusion of a reactant within the porous catalyst support. Values of $C_{WP} \ll 1$ indicate that the observed reaction is much slower than the rate of internal mass transfer, so the latter can be assumed to not be

limiting, whereas values of C_{WP} approaching unity or > 1 indicate that mass transfer may be limiting the observed reaction rate. For this study, C_{WP} is defined as:

$$C_{WP} = \frac{R^2 k_{obs,0} \tau}{D\theta} \tag{B.8}$$

where R is the radius of the catalyst support particle, τ is the tortuosity factor of the catalyst (typically varies from 2 to 10),[7] D is the diffusion coefficient of nitrate in bulk solution (1.7×10^{-9} m^2 s^{-1}),[8] and θ is the porosity of the catalyst particle (typically varies from 0.2 to 0.7).[9] The projected area of the particles was determined by optical microscope, and the radius R was estimated by treating the particles as spheres. A conservative estimate of the maximum value of C_{WP} was obtained by choosing the smallest θ (0.2), largest τ (10), and maximum R (66 μm). The resulting C_{WP} estimate of 0.18 is $\ll 1$ when nitrate is reacted with the highest Ru/C loading tested (0.5 g L^{-1}), indicating that internal mass transfer is not limiting.[6, 10] It is inferred that mass transfer limitation is not significant for Al_2O_3 supported catalysts for the reason that Al_2O_3 supports have much larger pore size than C supports and smaller $k_{obs,0}$ values (Table B.1).
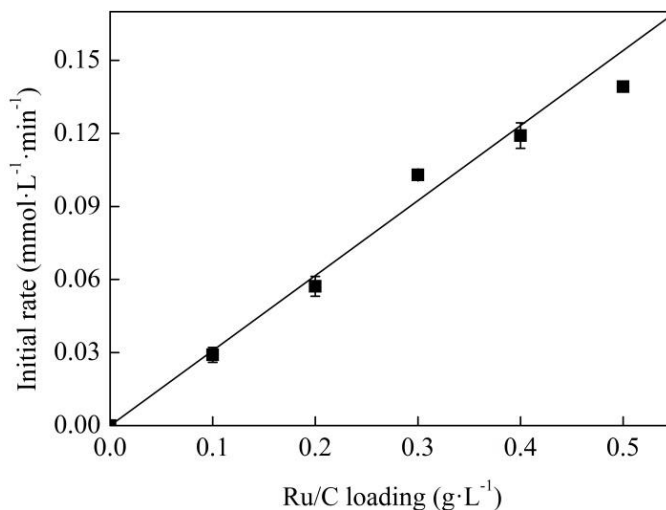
Figure B.2 Influence of 5 wt% Ru/C catalyst loading in the aqueous suspension on the initial rate of nitrate reduction (1 atm H_2 continuous sparging, pH 5.0 maintained by automatic pH stat, 25 $\pm$ 0.5 °C, $[NO_3^-]_0 = 1.6$ mM). Error bars represent standard deviations of triplicate reactions.

B.2.2 Experimental results
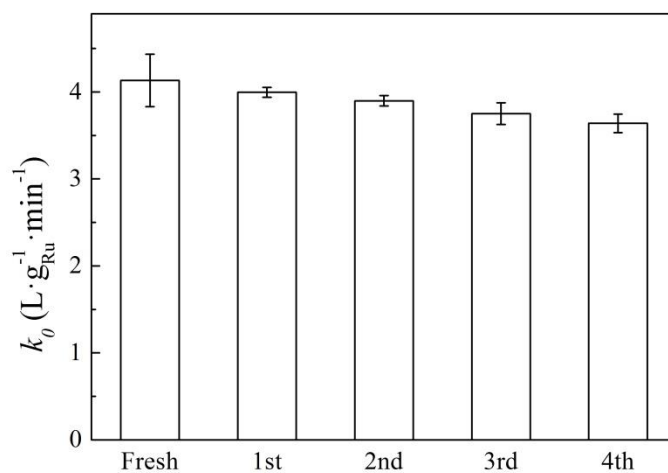
Figure B.3 Re-use of Ru/C in semi-batch system. Error bar for fresh catalyst represents standard deviations of triplicate reactions. For reuse experiments, error bars represent the min/max values measured in duplicate reactions.
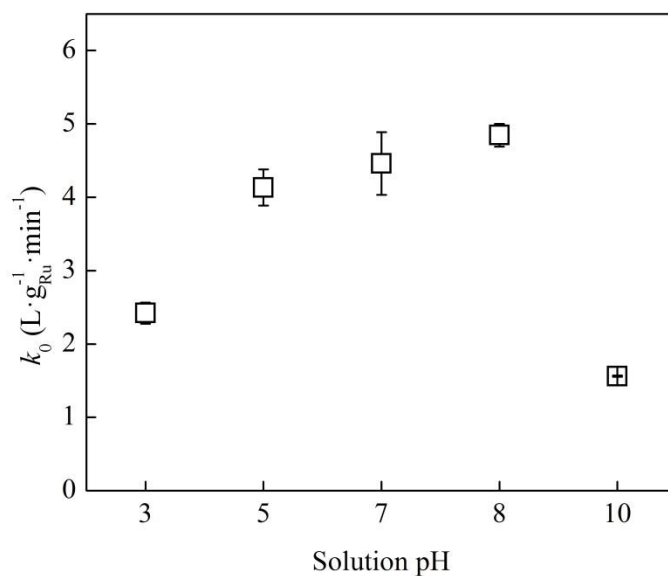
Figure B.4 Influence of pH on the Ru-mass-normalized pseudo-first-order rate constants for nitrate reduction on Ru/C (1 atm H_2 continuous sparging, 25 ± 0.5 °C, 0.2 g L^{-1} Ru/C, $[NO_3^-]_0 =$ 1.6 mM). Error bars represent standard deviations of triplicate reactions.
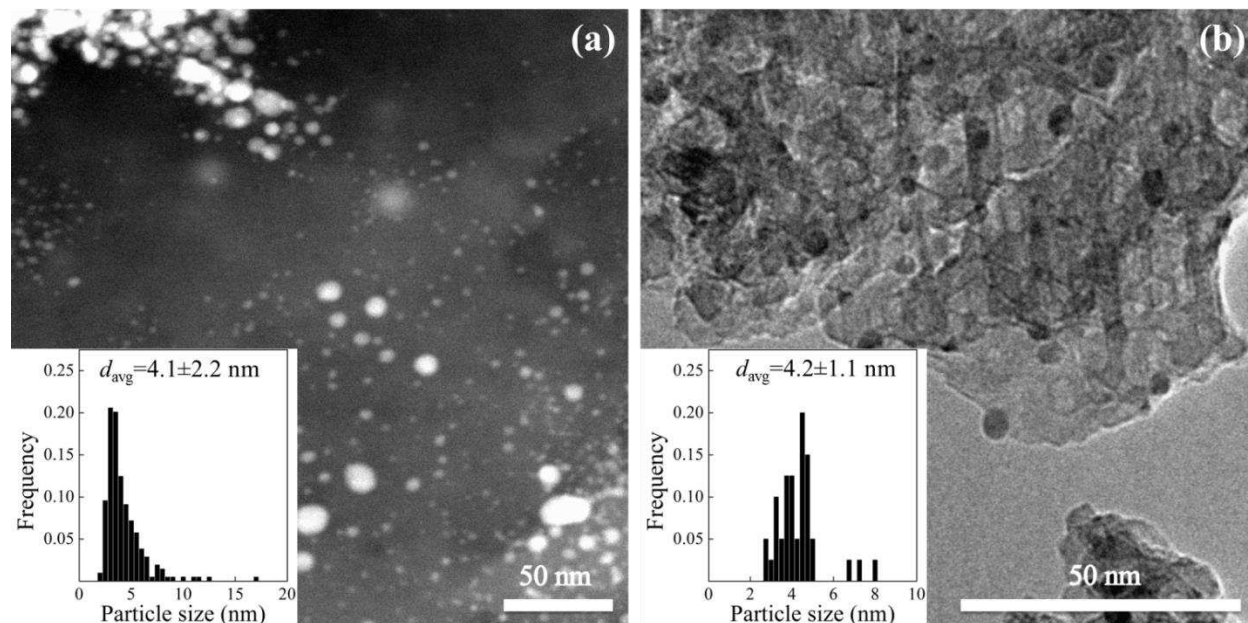
Figure B.5 (a) HAADF-STEM image of *ex situ* H_2 pretreated Pd/C and (b) TEM image of *ex situ* H_2 pretreated Pd/Al$_2$O$_3$. The insets show Pd particle size distributions.

Table B.1 Nitrate reduction activity of Pd-Cu and Ru catalysts in batch reactor and using H_2 as a reductant.

Catalyst	T (°C)	$[NO_3^-]_0$ (mM)	Initial rate (mmol $g_{Pd/Ru}^{-1}$ min^{-1})[a]	Ref.
4.7 wt% Pd-1.4 wt% Cu/γ-Al$_2$O$_3$	20	1.6	5.2	[11]
5 wt% Pd-1.25 wt% Cu/C	25	1.5	9.9	[12]
5 wt % Pd-1.5 wt % Cu/γ-Al$_2$O$_3$	21	2.1	10.8	[13]
5 wt% Pd-1 wt% Cu/C	25	1.6	0.6	[14]
2.8 wt % Pd-1.6 wt % Cu/α-Fe$_2$O$_3$	25	2.1	2.0	[15]
5 wt% Pd-1 wt% Cu/C	25	1.6	6.7	This study
5 wt% Ru/C	25	1.6	6.7	This study
5 wt% Ru/Al$_2$O$_3$	25	1.6	1.5	This study

[a]In the case that rate constant instead of reaction rate was reported, the initial reaction rate was calculated by multiplying the first-order rate constant by the initial nitrate concentration.

Table B.2 Surface and bulk properties of Ru catalysts from chemisorption analyses.

Catalyst		Active surface (%)	H_2 consumption (μmol$_{H2}$ μmol$_{Ru}^{-1}$)[a]
Ru/C	As-received	11	2.63
	N$_2$ pretreated	33	2.13
	H$_2$ pretreated	32	2.09
Ru/Al$_2$O$_3$	As-received	0	2.24
	N$_2$ pretreated	0	2.01
	H$_2$ pretreated	9	0.33

[a]Calculated from the major peak below 400 °C of the TPR profile.
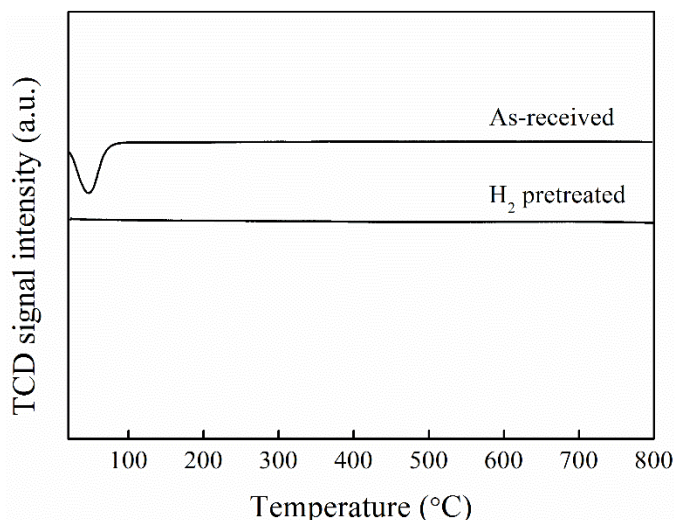
Figure B.6 Temperature-programmed desorption profile of Ru/C.

Table B.3 TOF$_0$ of nitrate reduction and nitrite reduction measured in mixture of nitrate and nitrite added to Ru/C reactors with varying initial concentration ratio.

$[NO_3^-]_0$ (mM)	$[NO_2^-]_0$ (mM)	TOF$_0$-NO$_3^-$ (min^{-1})	TOF$_0$-NO$_2^-$ (min^{-1})
1.6	1.6	0.026 ± 0.003	0.26 ± 0.04
1.6	0.26	0.36 ± 0.03	0.95 ± 0.05
0.26	0.26	0.21 ± 0.01	1.3 ± 0.2
0.26	0	1.1 ± 0.1	
1.6	0	2.1 ± 0.2	
0	0.26		3.4 ± 0.2
0	1.6		0.73 ± 0.06

B.2.2   DFT calculation notes and results

DFT calculations were carried out to describe the thermodynamic favorability of the reactions taking place in the experimental systems. A Ru$_{18}$ cluster was kept rigid during the optimization of various small molecular adsorbed species. As a result, some small imaginary frequencies were observed, which were ignored. The Ru$_{18}$ structure was optimized to a true minimum (no imaginary frequencies). To limit the effect of imaginary frequencies on the results, only the bottom of the well (HF energies) were utilized to calculate adsorption energies and compute the thermodynamic favorability of proposed reactions pathways. Additionally, surface

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conformations showing imaginary frequencies larger than 150 cm^{-1} or showing multiple (4 or greater) imaginary frequencies were immediately disqualified from the mechanism. Furthermore, multiple conformations were optimized for a variety of individual molecular species, including edge bond moieties. To maintain consistency, edge bound species were omitted from the analysis.

Given the computational methods and assumptions within this study, we want to emphasize the qualitative or semi-quantitative nature of the results. Additionally, all Ru$_{18}$ clusters were optimized as restricted ground state singlets, with all electrons paired. For additional consistency, reactions involving reductions by a hydrogen atom assumed to proceed via surface absorbed hydrogen atoms. The same strategy was used when H$_2$O is produced in a reaction. However, acidic protons were modeled by a bulk solvated H$_3$O$^+$ molecule unbound to the surface. No significant difference was observed when a free implicitly solvated H-atom was used to calculate reaction energetics. Similar strategy was used when H$_2$O was evolved in certain reactions; H$_2$O was treated as an unbound, implicitly solvated water molecule. Finally, hydrogen ions (H$^+$) were approximated by the difference between H$_2$O and H$_3$O$^+$ complexes.

Spin contamination was present in the optimization of many complexes containing unpaired electrons. As a result, ROPBE0 HF energies were computed with single point calculations using geometries obtained at the spin contaminated UPBE0 level.

Table B.4 Adsorption energies (eV) of nitrogen species (major reactants, hypothesized intermediates, and products) on Ru$_{18}$ clusters.[a]

Species	ΔE_{ads} (eV)
Ru$_{18}$-NO$_3^-$	-1.2
Ru$_{18}$-NO$_2^-$	-1.3
Ru$_{18}$-NO$_2$	-3.3
Ru$_{18}$-NO	-2.0
Ru$_{18}$-N$_2$O	-1.7
Ru$_{18}$-NH$_3$	-0.97
Ru$_{18}$-N$_2$	-1.4
Ru$_{18}$-H$_2$O	-1.1
Ru$_{18}$-H	-1.9

Table B.5 Energetics of the most thermodynamically favorable reaction pathways for aqueous nitrate reduction on Ru_{18} clusters.

Reaction steps	ΔE (eV)
Sequential reduction of NO_3^- to NO	
$NO_3^-{}_{ads} + 2H_{ads} \rightarrow NO_2^-{}_{ads} + H_2O_{ads}$	-3.5
$NO_2^-{}_{ads} + H_{ads} + H^+ \rightarrow NO_{ads} + H_2O_{ads}$	-5.6
Sequential reduction of NO to NH_3	
$NO_{ads} + H_{ads} \rightarrow HNO_{ads}$	-1.1
$HNO_{ads} + H_{ads} \rightarrow H_2NO_{ads}$	-0.8
$H_2NO_{ads} + H_{ads} \rightarrow H_2NOH_{ads}$	-0.9
$H_2NOH_{ads} + H_{ads} \rightarrow NH_2{}_{ads} + H_2O_{ads}$	-2.8
$NH_2{}_{ads} + H_{ads} \rightarrow NH_3{}_{ads}$	-1.4
N-N coupling and N_2 production	
$NO_{ads} + NO_2^-{}_{aq} \rightarrow N_2O_3^-{}_{ads} + H_2O_{ads}$	-1.3
$N_2O_3^-{}_{ads} + 2H_{ads} \rightarrow N_2O_2^-{}_{ads} + H_2O_{ads}$	-3.1
$N_2O_2^-{}_{ads} + H_{ads} H^+ \rightarrow N_2O_{ads} + H_2O_{ads}$	-6.3
$N_2O_{ads} + 2H_{ads} \rightarrow N_2{}_{ads} + H_2O_{ads}$	-4.9

B.2.3 References

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APPENDIX C

SUPPLEMENTARY DATA FOR CHAPTER 4

C.1   Evaluation of Internal Mass Transfer Limitation

The Weisz-Prater parameter (C_{WP}) was estimated to evaluate internal mass transfer limitations.[1] It provides a measure of the characteristic time scale of an observed reaction in comparison to the estimated characteristic time for internal diffusion of a reactant within the porous catalyst support. Values of $C_{WP} \ll 1$ indicate that the observed reaction is much slower than the expected rate of internal mass transfer, so the latter can be assumed to not be limiting, whereas values of C_{WP} approaching unity or >1 indicate that internal mass transfer may be limiting the observed reaction rate. For this study, C_{WP} is defined as:

$$C_{WP} = \frac{R^2 k_{obs,0} \tau}{D\theta} \qquad (C.1)$$

Where R is the radius of the catalyst support particle, τ is the tortuosity factor of the catalyst (typically varies from 2 to 10),[2] D is the diffusion coefficient of NDMA in bulk solution ($9.64 \times 10^{-10}\,\text{m}^2\,\text{s}^{-1}$)[3] and θ is the porosity of the catalyst particle (typically varies from 0.2 to 0.7).[4] The projected area of the particles was determined by optical microscope, and the radius R was estimated by treating the particles as spheres. A conservative estimate of the maximum value of C_{WP} was obtained by choosing the smallest θ (0.2), largest τ (10), and maximum R (101 µm). The resulting C_{WP} estimate of 0.16 is $\ll 1$ under standard testing conditions ($[\text{NDMA}]_0 = 100$ µM, 0.1 g L^{-1} Ru/Al$_2$O$_3$), indicating that internal mass transfer is not rate limiting.[1, 5]

C.2   Experimental Results

Table C.1 Composition of dechlorinated tap water.

Component	Concentration
Alkalinity	35.6 mg L^{-1} as CaCO$_3$
TDS	202 mg L^{-1}
Chloride	27.7 mg L^{-1} as Cl$^-$
Nitrate	1.2 mg L^{-1} as NO$_3^-$
Nitrite	ND[a]
Sulfate	90.8 mg L^{-1} as SO$_4^{2-}$
Phosphate	ND[a]
Ca	29.8 mg L^{-1}
Mg	7.0 mg L^{-1}
Fe	ND[a]
Mn	ND[a]
TOC	1.3 mg L^{-1}
Ammonia	<0.02 mg L^{-1} NH$_3$-N
pH	7.6

[a]Not detected
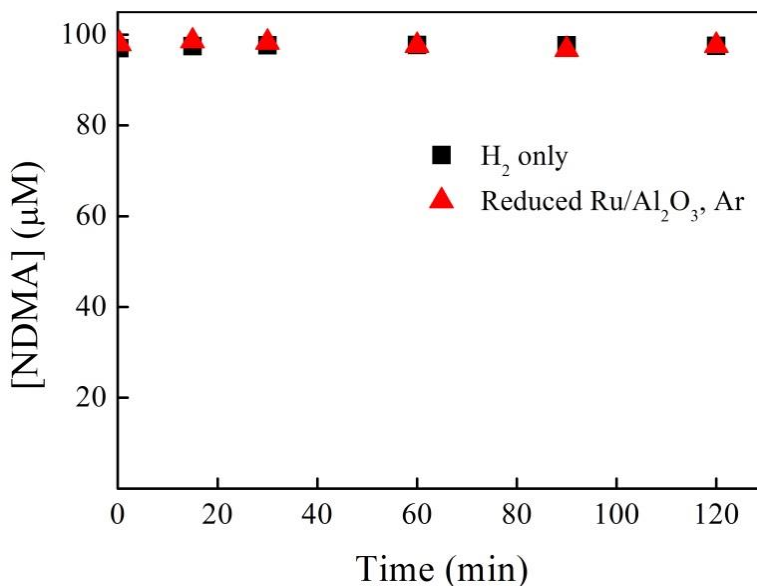
Figure C.1 Control experiments for NDMA reaction in H$_2$-sparged solution (no catalyst) and suspensions of commercial Ru/Al$_2$O$_3$ catalyst sparged with Ar (inert gas) in place of H$_2$. Error bars representing the range of values measured in duplicate reactions are all smaller than symbols shown.

Table C.2 NDMA reduction activity and products over different catalysts.

Catalyst	Catalyst dose	$[NDMA]_0$ (μM)	Metal weight normalized pseudo-first-order rate constant	Organic product	Inorganic product	Ref.
1%Pd/γ-Al$_2$O$_3$	10 mg$_{Pd}$ L^{-1}	1.4	11.5 ± 0.9 L g$_{Pd}^{-1}$ h^{-1}	DMA	-[a]	[4]
1%Pd0.3%Cu/γ-Al$_2$O$_3$	10 mg$_{me}$ L^{-1} [b], 3 mg$_{Cu}$ L^{-1}	1.4	66.5 ± 7.4 L g$_{me}^{-1}$ h^{-1} [b]	DMA	-[a]	[4]
5%Pd1%In/γ-Al$_2$O$_3$	5.5 mg$_{Pd}$ L^{-1}, 1.0 mg$_{In}$ L^{-1}	1.4	45.3 ± 3.6 L g$_{Pd}^{-1}$ h^{-1}	DMA	Ammonia	[6]
2.4%Pd0.6%Ni/γ-Al$_2$O$_3$	3.6 mg$_{Pd}$ L^{-1}, 0.9 mg$_{Ni}$ L^{-1}	2	836 ± 21 L g$_{me}^{-1}$ h^{-1} [b]	DMA	-[a]	[7]
Low surface area Ni	10 mg$_{Ni}$ L^{-1}	1.4	8.3 ± 2.9 L g$_{Ni}^{-1}$ h^{-1}	DMA	-[a]	[4]
Raney Ni	435 mg$_{Ni}$ L^{-1}, 40 mg$_{Al}$ L^{-1}	100	77.9 ± 13.1 L g$_{Ni}^{-1}$ h^{-1}	DMA	N$_2$	[3]
NiB	425 mg$_{Ni}$ L^{-1}, 35 mg$_B$ L^{-1}	100	29.5 ± 2.4 L g$_{Ni}^{-1}$ h^{-1}	DMA	Ammonia	[8]
5%Pd/Al$_2$O$_3$	4.6 mg$_{Pd}$ L^{-1}	100	3.9 ± 1.3 L g$_{Pd}^{-1}$ h^{-1}	Not analyzed	Not analyzed	This study
5%Pd1%In/Al$_2$O$_3$	4.6 mg$_{Pd}$ L^{-1}, 0.87 mg$_{In}$ L^{-1}	100	23.9 ± 5.1 L g$_{Pd}^{-1}$ h^{-1}	Not analyzed	Not analyzed	This study
Commercial 5%Ru/Al$_2$O$_3$	4.5 mg$_{Ru}$ L^{-1}	100 Low[c] 0.014[d]	1103 ± 133 L g$_{Ru}^{-1}$ h^{-1} 5030 L g$_{Ru}^{-1}$ h^{-1} [c] 5700 ± 490 L g$_{Ru}^{-1}$ h^{-1} [d]	DMA	Ammonia	This study
In-house 5%Ru/Al$_2$O$_3$	4.6 mg$_{Ru}$ L^{-1}	100	2718 ± 321 L g$_{Ru}^{-1}$ h^{-1}	Not analyzed	Not analyzed	This study

[a]Ammonia was not detected potentially due to the limitation of detection method, and N$_2$ was not measured.

[b]Metal is not specified.

[c]Extrapolation from Langmuir-Hinshelwood model to linear region.

[d]From test of five *N*-nitrosamines mixed in tap water.

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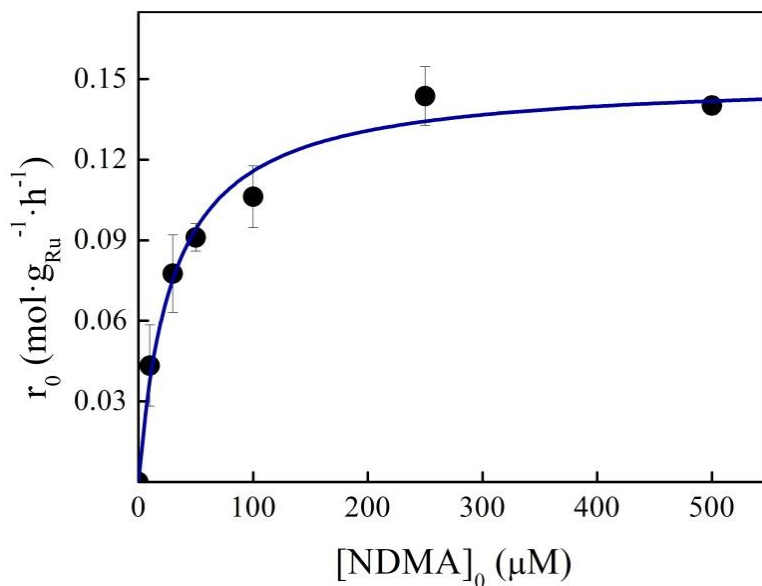
Figure C.2 Initial reaction rate as a function of initial NDMA concentration. Lines represent least-squares fit of Langmuir-Hinshelwood model to the data shown. Error bars represent standard deviations of triplicate experiments.
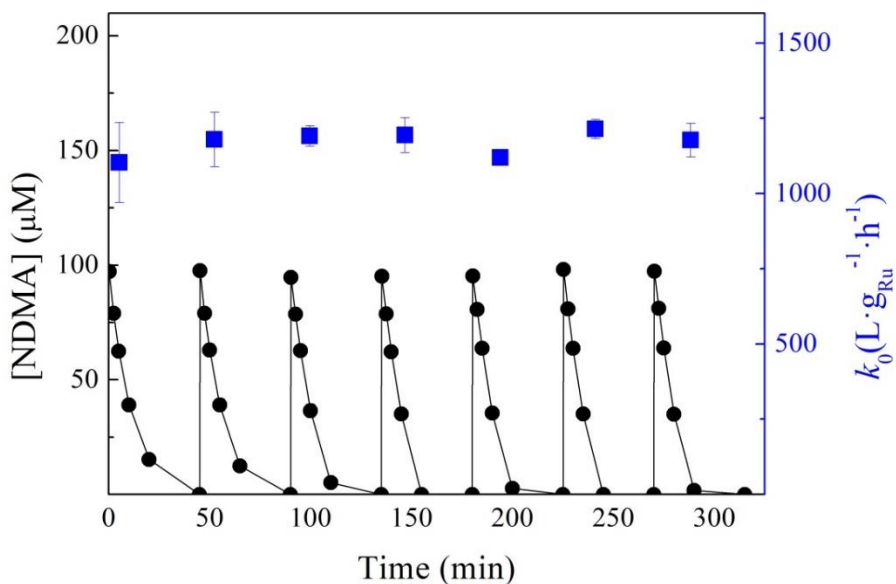
Figure C.3 NDMA reduction activity of commercial Ru/Al$_2$O$_3$ in repetitive NDMA spiking experiments (0.1 g L^{-1} catalyst, pH 6.0 buffered by 10 mM MES buffer, continuous sparging of 1 atm H$_2$, 22 ± 0.5 °C). Error bars represent range of results from duplicate reactions (smaller than symbol if not visible).
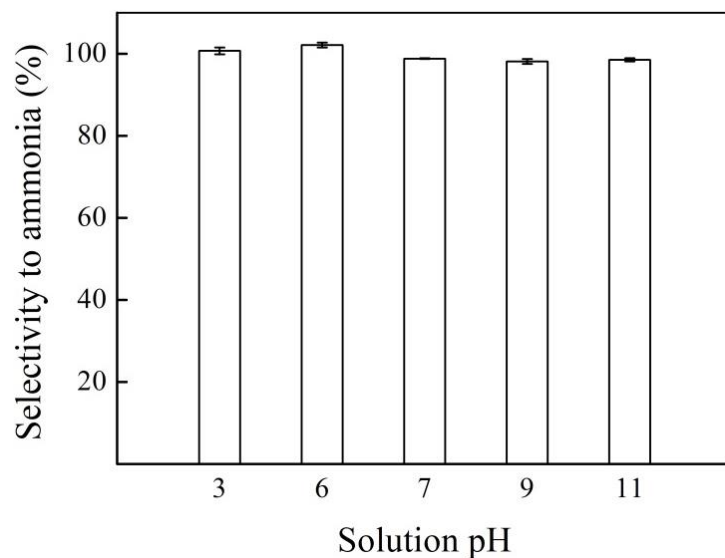
Figure C.4 NDMA reduction product selectivity to ammonia as a function of solution pH. Error bars represent the range of observed values in duplicate experiments.
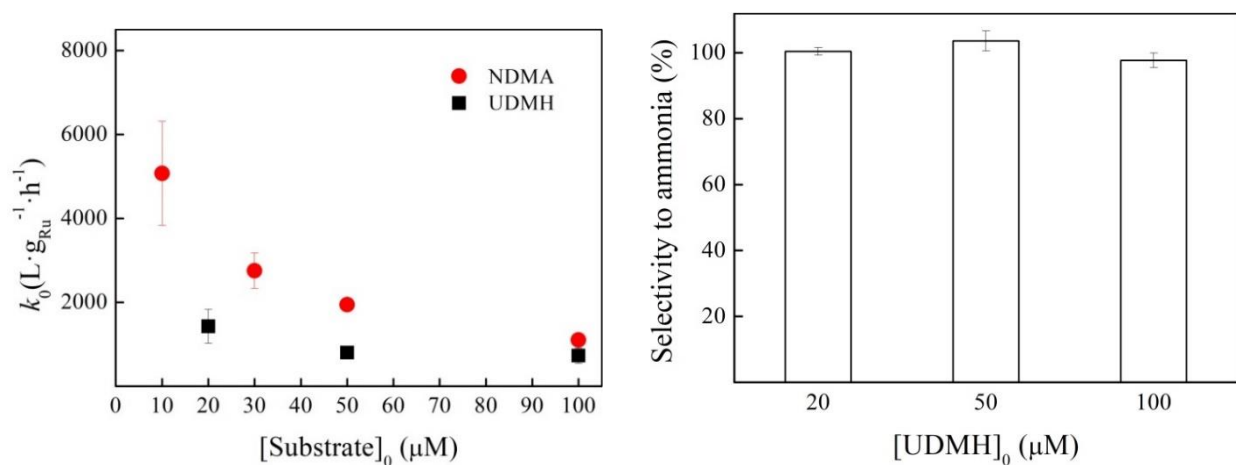
Figure C.5 (A) Comparison of metal weight-normalized pseudo-first-order rate constants for reduction of NDMA and UDMH, and (B) UDMH reduction product selectivity as a function of initial UDMH concentration in the semi-batch reactor system (0.1 g L^{-1} catalyst, pH 6.0 buffered by 10 mM MES buffer, continuous sparging of 1 atm H$_2$, 22 ± 0.5 °C). Error bars represent standard deviations obtained from triplicate experiments.
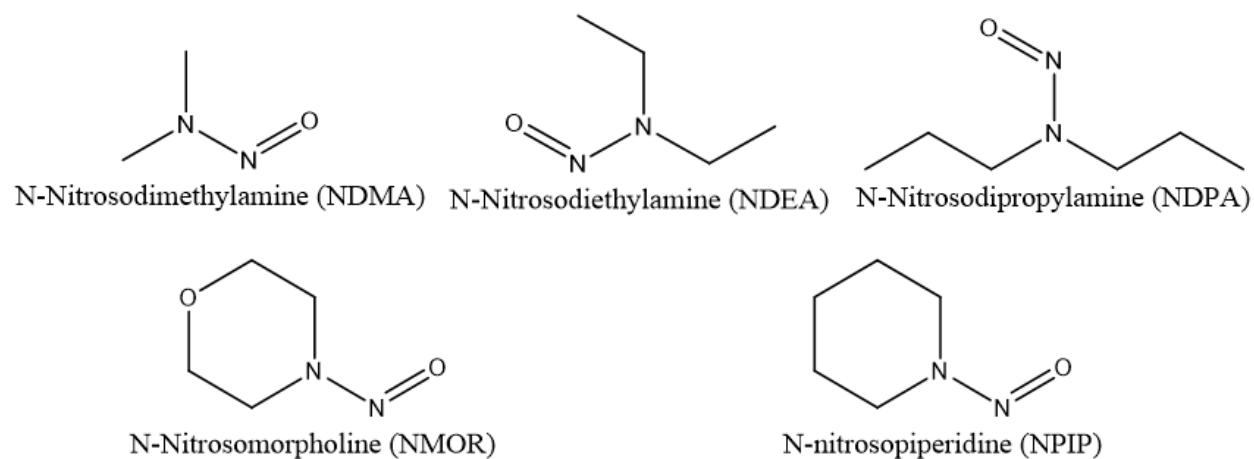
Figure C.6 Structures of *N*-nitrosamines examined in treatment experiments conducted in tap water.
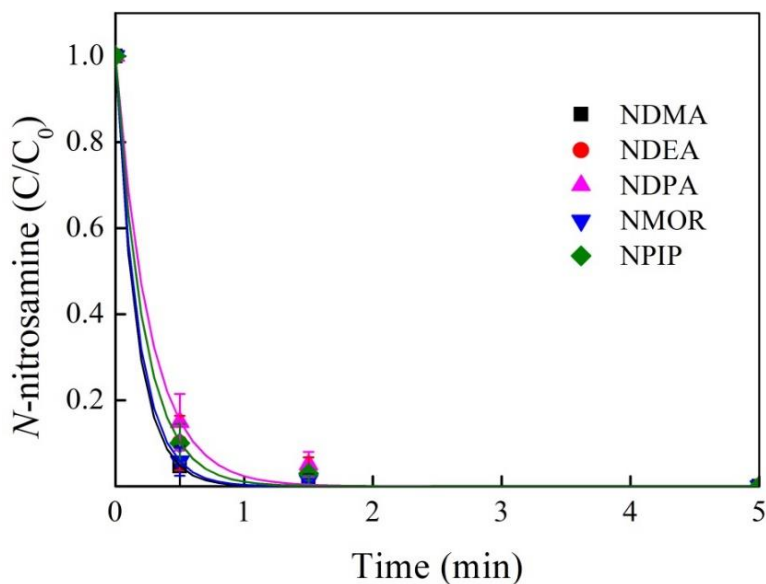
Figure C.7 Catalytic reduction of a mixture of *N*-nitrosamines added to deionized water (1 ug L^{-1} of each *N*-nitrosamine, 0.1 g L^{-1} commercial Ru/Al$_2$O3 catalyst, initial solution pH 9.0, continuous sparging of 1 atm H$_2$, 22 $\pm$ 0.5 °C). Error bars represent the range of measured values in duplicate reactions (smaller than symbol if not visible).

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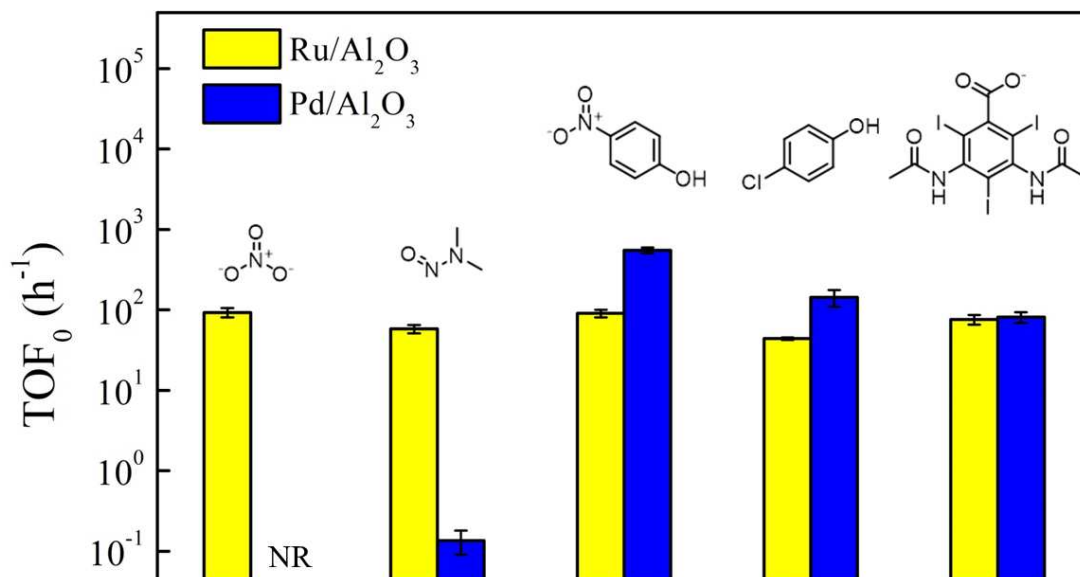
Figure C.8 Comparison between Ru/Al$_2$O$_3$ and Pd/Al$_2$O$_3$ catalyst activities for reduction of different N-containing contaminants and halogenated aromatic contaminants. Error bars represent standard deviations of triplicate reactions. Data for NO$_3^-$ from previous study.[9]

C.3   References

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SUPPLEMENTARY DATA FOR CHAPTER 5
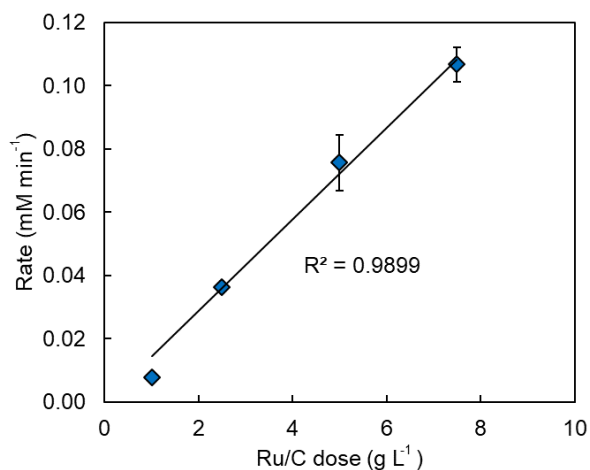
Figure D.1 Initial nitrate hydrogenation rate as a function of Ru/C loading. Conditions: Initial $[NO_3^-]$ = 100 mM, brine matrix (5 wt% NaCl, 100 mM $NaHCO_3$, 100 mM Na_2SO_4), 30 °C, no solution pH control, 1 atm H_2 headspace maintained by flowing H_2 at ca. 300 mL min^{-1}. Error bars indicate standard deviation from duplicate measurements (smaller than symbol if not visible).
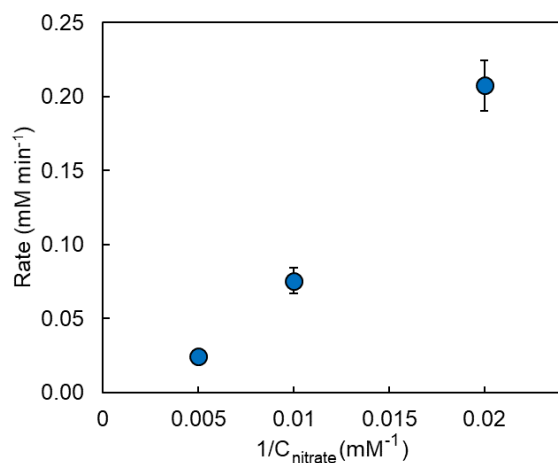
Figure D.2 Plot of initial rate versus the inverse of initial nitrate concentrations. Error bars indicate standard deviation from duplicate measurements (smaller than symbol if not visible).

APPENDIX E

SUPPLEMENTARY DATA FOR CHAPTER 6

E.1   Experimental Methods

E.1.1   Catalyst synthesis and characterization

Pt/Al$_2$O$_3$ catalyst was prepared by strong electrostatic adsorption method with chloroplatinic acid hexahydrate as Pt precursor. Al$_2$O$_3$ of 30-50 mesh and Pt precursor were added to deionized water, and solution pH was adjusted to 3 by adding HCl. After stirring overnight, the catalyst particles were recovered by filtration extensively washed with deionized water. The catalyst was dried in the air and reduced in flowing H$_2$ (200 mL min^{-1}) at 300 °C for 4 h.

BET surface area was determined by nitrogen physisorption using a Quadrasorb SI™ surface area analyzer from Quantachrome Instruments. Samples of ~80–120 mg were measured using a 55-point nitrogen adsorption/desorption curve at -196 °C. Prior to analysis, the samples were degassed at 300 °C for 16 h under vacuum. BET surface areas were calculated over a relative pressure range of 0.050 to 0.250 P/P$_0$. The surface area measurements are within 10% of deviation.

Pt dispersion on alumina was measured from CO pulse chemisorption performed using an Altamira AMI-390 micro-flow reactor system equipped with a thermal conductivity detector (TCD). Samples of ~50–100 mg were loaded in a quartz U-tube reactor and heated in 5% H$_2$/Ar to 250 °C at 5 °C min^{-1} with a hold time of 2 h. After the reduction step, catalyst samples were flushed with He at 50 mL min^{-1} for 1 h, cooled to 30 °C and dosed with sequential 500-µL pulses

of 10% CO/He mixture. A 500-μL sample loop was used to calibrate the TCD response for CO after each experiment. Pt dispersion was calculated by assuming a Pt:CO stoichiometry of one-to-one.

The total number of acid sites was determined by NH_3 pulse chemisorption using the same Altamira Instruments AMI-390 system. Samples of ~100–150 mg were loaded in a quartz U-tube reactor. ZrO_2 samples were pretreated under flowing He at 5 °C min^{-1} to 350 °C and then held at this temperature for 2 h. Nb_2O_5 samples were pretreated under flowing He at 5°C min^{-1} to 300 °C with a hold time of 2 h. Pt/Al_2O_3 samples were pretreated under flowing 5% H_2/Ar to 300 °C at 5 °C min^{-1} with a hold time of 2 h. The samples were cooled to 120 °C under flowing He and dosed with sequential 2000-μL pulses of 10% NH_3/He mixture. A 2000-μL sample loop was used to calibrate the TCD response for NH_3 after each experiment.

The relative ratio of Brønsted to Lewis acid sites was determined by pyridine adsorption diffuse reflectance Fourier transform infrared spectroscopy (py-DRIFTS). Spectra represent the average of 64 scans collected at 4 cm^{-1} resolution using a Thermo Nicolet iS50 FT-IR spectrometer equipped with a Harrick Praying Mantis reaction chamber. Oxide samples were pretreated under flowing Ar at 5°C min^{-1} to 350 °C and then held at this temperature for 2 h. Pt/Al_2O_3 samples were pretreated under flowing 5% H_2/Ar to 300 °C at 5°C min^{-1} with a hold time of 2 h. After cooling to 150 °C at 5 °C min^{-1}, the samples were purged with Ar for 10 min, and a background spectrum was collected. The samples were then exposed to pyridine vapor for 5 min by flowing Ar through a pyridine-filled bubbler held at room temperature. Physisorbed pyridine was subsequently desorbed in Ar by heating to 200°C at 5°C min^{-1} and holding for 30 min. After cooling to 150 °C at 5°C min^{-1}, a spectrum was collected and referenced to the background collected prior to pyridine exposure. The peak area of vibrational modes near 1445

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cm^{-1} (Lewis) and 1540 cm^{-1} (Brønsted) were used to determine the relative ratio of Brønsted to Lewis acidic sites.

The irreversibly adsorbed carbon amount of spent catalysts was measured by a Setaram Setsys Evolution thermal gravimetric analyzer (TGA) coupled with a Nicolet 6700 Fourier Transform InfraRed (FTIR) spectrometer via a transfer line heated at 200 °C. The FTIR spectrometer is equipped with a gas cell maintained at 225°C to prevent vapor condensation. The catalyst was heated to 800 °C under zero air (19-21% oxygen with a balance of nitrogen). The onset of carbon combustion was determined by the observation of carbon dioxide in the FTIR. Prior to the onset of carbon combustion, only water was observed in the FTIR spectra. Therefore, the carbon content was calculated by subtracting the mass loss due to water from the total mass loss recorded by the TGA.

E.1.2 Catalytic testing

Acid ketonization experiments were carried out in packed-bed reactor at 435 °C and atmospheric pressure. The liquid flow and Ar flow rates were 0.2 mL min^{-1} and 100 mL (STP) min^{-1}, respectively. The feed was introduced to the reactor by a HPLC pump. Both the liquid feed and Ar flew downward through a ZrO$_2$ catalyst (Johnson Matthey, 30-50 mesh) bed in between inert 1-mm glass beads, which were held in place with quartz wool in a 0.5" OD (0.035" wall thickness) tubular stainless-steel reactor coated with a silica Dursan coating (SilcoTek Coating Co.). The reactor was heated by a tubular split furnace. A back-pressure regulator was used to control the reactor pressure (the regulator was fully open for ketonization experiments). Liquid products were collected in a knock-out pot and analyzed off-line. The gaseous products were monitored by an on-line gas chromatograph and a nondispersive infrared detector. Conversion and carbon yield are defined by the following equations:

$$\text{Conversion} = \frac{f_{\text{Reactant, feed}} - f_{\text{Reactant, ave}}}{f_{\text{Reactant, feed}}} \times 100\% \tag{E.1}$$

$$\text{Carbon yield} = \frac{f_{\text{Product,ave}}}{f_{\text{Reactant, feed}}} \times 100\% \tag{E.2}$$

where $f_{\text{Reactant, feed}}$ = molar flow rate of carbon in reactant in the feed; $f_{\text{Reactant,ave}}$ = average molar flow rate of carbon in reactant during sampling interval; $f_{\text{Product, ave}}$ = average molar flow rate of carbon in product during sampling interval.

Ketone condensation experiments were performed in a Parr multi-batch reactor system (Parr Instrument Co.). Feed solution and Nb_2O_5 catalyst (CBMM, calcined in air at 350 °C for 12 h) were added to 75-mL reactor cups, followed by purging and flushing of the system with He for three cycles. The reactors were sealed and heated to the desired temperature over a period of ~20 min. Reaction solution and catalyst were well mixed by using magnetic stir bars operating at 800 rpm. Reactors were quenched in an ice bath to terminate the reaction at predetermined time. Products were filtered through 0.2-μm PTFE membranes to separate the liquid from the catalysts. Conversion, average rate, carbon yield and selectivity are defined by the following equations:

$$\text{Conversion} = \frac{n_{\text{Reactant, initial}} - n_{\text{Reactant,t}}}{n_{\text{Reactant, initial}}} \times 100\% \tag{E.3}$$

$$\text{Average rate} = \frac{n_{\text{Reactant, initial}} - n_{\text{Reactant,t}}}{m_{\text{Catalyst}} \times t} \times M_{\text{Reactant}} \tag{E.4}$$

$$\text{Yield} = \frac{n_{\text{Product,t}}}{n_{\text{Reactant, initial}}} \times 100\% \tag{E.5}$$

$$\text{Selectivity} = \frac{\text{Carbon yield}}{\text{Conversion}} \times 100\% \tag{E.6}$$

where $n_{\text{Reactant,initial}}$ = mole of carbon in reactant in the feed; $n_{\text{Reactant,t}}$ = mole of carbon in reactant at a given time; m_{Catalyst} = mass of catalyst; t = reaction time; M_{Reactant} = the molar mass of reactant; $n_{\text{Product,t}}$ = mole of carbon in product at a given time.

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To prepare feed for HDO, the liquid product from condensation experiments were distilled by using spinning band distillation. Solvent and unreacted ketone were recycled to condensation reaction during process integration experiments. Purified condensation products were directly used as feed, with exception of biologically derived condensation products. Due to limited quantity, bioderived condensation products were mixed with cyclohexane at 20 wt%. HDO experiments were carried out at 334 °C and under a H_2 pressure of 500 psi over a Pt/Al_2O_3 catalyst (30-50 mesh) in the same flow reactor where ketonization experiments were performed. The liquid flow and H_2 flow rates were 0.1 mL min^{-1} and 165 mL (STP) min^{-1}, respectively.

E.1.3 Chemical analysis

For GC-FID/MS, samples were analyzed using an Agilent 7890A GC operating in split mode (25:1 split ratio). The GC was outfitted with an Agilent HP-5ms column (30 m × 0.25-mm id, 0.25-µm film), and helium was used as the carrier gas at 1.4 mL min^{-1} column flow. The injector volume was set to 1 µL using an Agilent auto-sampler. The GC method consisted of a front inlet temperature of 260°C and an oven temperature program that starts at 40°C, holding for 2 min and then ramping at 18°C min^{-1} to a temperature of 280 °C before cooling down. Sample was analyzed simultaneously by a Polyarc® system/FID and 5975 mass spectrometer detector (Agilent Technologies). FID was set at 300°C, H_2 flow at 30 mL min^{-1}, air flow at 350 mL min^{-1}, and makeup flow at 20 mL min^{-1}. MS transfer line temperature was set at 293 °C.

High resolution mass spectra were collected using a JEOL GCmate II double-focusing mass spectrometer (JEOL, Peabody, MA) coupled with a DSC/TGA Q600 (TA Instruments, Newcastle, DE). Liquid samples were introduced to the MS via a heated transfer line and evaporated by heating in the DSC/TGA instrument to their boiling point. Calorimetric data were not collected as the aim of these experiments were to collect mass spectra of volatilized

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compounds only. The ionization source was operated in electron ionization (EI) mode at 70 eV. The mass spectrometer was tuned prior to experiments to a resolving power of ≥6,000 (full width at half maximum (FWHM)) based on m/z 69 using the spectrum of perfluorokerosene. The full spectrum of perfluorkerosene was used for mass calibration across the range of the spectrum collected from m/z 35 to 400.

Quantitative ^{13}C NMR spectra were acquired with ~400 μL sample and included a capillary tube filled with 1 mg/mL TSP-d_4 in DMSO-d_6 for referencing. Experiments were run using a Bruker AVANCE III 600 MHz spectrometer (14.7 T) equipped with a room temperature BBO (broad band optimized) 5 mm probe head. All spectra were measured at 25 °C using a 90° pulse angle, inverse-gated decoupling, 2048 scans, and a delay of either 10 or 30 s. Integrations were performed on phased and baseline-corrected spectra, with solvent peaks excluded. Distortionless Enhancement by Polarization Transfer (DEPT) experiments were run with selection angle parameter of 135° which in CH and CH_3 groups as positive peaks, and CH_2 groups as negative peaks. The coupling constant, JCH, was set to 145 Hz. All data analysis was performed in Topspin 3.6pl7.

GCxGC-TOFMS was performed with LECO Pegasus® 4D GCxGC-TOFMS operating in split mode (50:1 split ratio). The GC was outfitted a Restek RTX-5 column (10 m × 0.15-mm id, 0.18-μm film) as the primary column and an Agilent DB1701 column (1 m × 0.10-mm id, 0.10-μm film) as the secondary column. Helium was used as the carrier gas at 1.0 mL min^{-1}. The injector volume was set to 1 μL using a Gerstel MPS2® autosampler, and the inlet temperature was set at 300°C. The primary oven temperature was held at 35 °C for 7 min, ramped at 5 °C min^{-1} to 255 °C and held for 1 min. The primary oven temperature was held at 35°C for 7 min, ramped at 5 °C min^{-1} to 255 °C and held for 1 min. The secondary oven temperature was set

10 °C offset from the primary oven, held for 4 min, ramped at 5 °C min^{-1} to 275°C and held for 2 min. Modulator Temperature was set 15 °C offset from the secondary oven and tracking the secondary oven program. Modulator Time was set at 6 s modulation, 1.0 s hot pulse / 2.0 s cold pulse. The MS setting consisted of MS transfer line temperature of 250°C and scan range from 29 m/z to 350 m/z at 200 spectra s^{-1}. ChromaTOF® data acquisition software was used to collect the chromatograms.

E.1.4 Lignocellulosic sugars fermentation and acids separation

The production of corn stover hydrolysate from deacetylation and dilute-acid pretreatment was previously described.[1] The hydrolysate was concentrated via rotavapor to reach a sugar concentration of approximately 450 g L^{-1} (see composition in Table E.5) and stored at 4 °C. Prior the fermentation, the hydrolysate was diluted with fermentation media to achieve an initial sugar (glucose, xylose, arabinose, and galactose) concentration of 65 g L^{-1}. The fermentation media consisted of yeast extract (5 g L^{-1}), peptone (10 g L^{-1}), ammonium sulfate (3 g L^{-1}), KH_2PO_4 (3.26 g L^{-1}), $MgSO_4 \cdot 7H_2O$ (0.3 g L^{-1}), $CaCl_2 \cdot 2H_2O$ (0.02 g L^{-1}), $FeSO_4 \cdot 7H_2O$ (0.03 g L^{-1}), $MnSO_4 \cdot H2O$ (0.02 g L^{-1}), cysteine-HCl (0.5 g L^{-1}) and resazurin (1 mg L^{-1}). The organism utilized for sugars conversion to carboxylic acids was *Clostridium butyricum* (ATCC 19398). This strict anaerobic bacterium was stored in sealed glycerol stocks at -80 ℃ and revived anaerobically in sealed serum bottles containing Reinforced Clostridial media supplemented with 20 g L^{-1} glucose and 10 g L^{-1} xylose. Cultures were incubated for ~15 h in a rotary shaker at 37 ℃ and 150 rpm. Cells were then directly inoculated in two 10-L New Brunswick BioFlo®/CelliGen® 310 bioreactors (Eppendorf) at an initial optical density at 600 nm (OD$_{600}$) of 0.1. Nitrogen was sparged overnight (0.1 vvm) to ensure anaerobic conditions but the gas was turned off at ~7 h to reduce foaming issues. Fermentations were maintained at 37 ℃

and 100 rpm. The pH was initially adjusted at pH 7 and further controlled at pH 6 by the addition of 4 N NaOH to neutralize the acids. Antifoam 204 (Sigma-Aldrich) was added when required. Samples (2 mL) were taken periodically in aseptic conditions from the bioreactors to track bacterial growth (OD_{600}), sugar utilization, and acids production. The analytical methods to quantify these metabolites were previously described.[1]

To recover bio-butyric acid from the fermentation broth, cells were first removed by centrifugation at 12,000 × g during 10 min. Then, the supernatants were filtered through 0.8-0.2 µM Sartopore 2 XLG cartridges (Sartorius) and further pumped through a 10 kDa hollow fiber filter (GE Model #UFP-10-C-4X2MA) maintaining a head pressure of 10 psi. After filtration, the broth, pH 6.5, was loaded with 10% w/v activated carbon and stirred for 2 hours. The activated carbon was removed using a 1L 0.45µm a PES Nalgene Rapid-Flow filter. The filtrate, pH 7.5, was further processed in 900 g batches. Each batch was concentrated to 23% of its original mass by removing water using a rotary evaporator at 30mbar and 50°C. The concentrated broth was then acidified to pH <2 using 1 g H_2SO_4 (Sigma-Aldrich ACS reagent, 95.0-98.0%) per 10 g of concentrated broth. The acidified concentrated broth was then extracted twice, 1:1 v/v with ethyl acetate (Sigma-Aldrich ACS reagent ≥99.5%) in a separatory funnel. The organic phase was collected, and the ethyl acetate was removed on the rotary evaporator at 150mbar and 50 °C. The remaining concentrated acetic and butyric acids were further purified and separated by vacuum distillation. The spinning band distillation column (BR Instruments 800 micro fractional distillation system) was operated at 100mbar. 4 fractions were collected: impurities below 112 °C, acetic acid between 112-122°C, acetic and butyric acid mixture between 122-173 °C, butyric acid between 173-175 °C. The concentration of ethyl acetate, acetic acid, and butyric acid in each fraction was determined in parallel with ^{1}H NMR and HPLC. Mixing several

distillation fractions to obtain the desired purity and ratio of acetic and butyric acid produced the final purified mixed acid product.

E.2   Experimental Results

Table E.1 Model predictions of melting point, boiling point, flash point, lower heating value, cetane number, and yield sooting index (normalized to carbon number in parentheses) for mapped hydrocarbons.

No.	Structure	C No.	Melting point (°C)		Boiling point (°C)			Flash point (°C)		L-heating value (MJ/kg)			CN	YSI
			M1	M2	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10
Non-cyclic branched hydrocarbons														
1		6	-131	-106	63	56	71	-29	-29	45	48	45	37	40 (6.6)
2		10	-86	-55	155	152	173	29	34	45	47	44	46	63 (6.3)
3		10	-101	-67	155	138	173	29	34	45	47	44	41	68 (6.8)
4		14	-56	-20	246	221	255	76	87	44	47	44	48	91 (6.5)
5		8	-109	-80	109	106	125	0	3	45	47	45	41	48 (6.0)
6		8	-109	-80	109	106	125	0	3	45	47	45	44	48 (6.0)
7		8	-124	-92	109	91	125	0	3	45	47	45	32	52 (6.5)
8		10	-86	-55	155	152	173	29	34	45	47	44	40	59 (5.9)
9		10	-101	-67	155	138	173	29	34	45	47	44	38	63 (6.3)
10		12	-64	-32	201	194	216	58	65	44	47	44	45	71 (5.9)
11		12	-79	-43	200	181	216	57	65	44	47	44	44	75 (6.2)
12		12	-79	-43	200	181	216	57	65	44	47	44	43	75 (6.2)
Cyclic hydrocarbons														
13		9	-55	-45	148	134	150	26	29	44	46	44	29	81 (9.0)
14		15	8	20	280	249	272	109	119	44	46	44	35	125 (8.3)
15		15	4	17	276	244	272	106	116	44	46	44	32	121 (8.1)
16		21	67	74	408	331	359	188	207	44	46	44	30	161 (7.7)
17		9	-83	-58	143	140	150	23	26	44	46	44	28	76 (8.4)
18		15	-16	11	280	258	272	109	120	44	46	44	39	110 (7.3)
19		15	-29	0	266	243	272	99	110	44	46	44	29	127 (8.4)
20		21	39	50	403	334	359	185	204	44	46	44	32	161 (7.7)
21		11	-33	-21	193	178	196	55	60	44	46	44	37	87 (7.9)
22		11	-61	-34	188	184	196	51	57	44	46	44	38	87 (7.9)
23		13	-10	2	239	218	236	83	92	44	46	44	37	99 (7.6)
24		13	-38	-11	234	222	236	80	88	44	46	44	44	99 (7.6)
25		15	12	24	285	254	272	112	123	44	46	44	35	110 (7.3)
26		15	-20	7	275	253	272	105	116	44	46	44	38	116 (7.7)
27		17	31	41	326	282	304	137	151	44	46	44	34	127 (7.5)
28		17	3	28	321	286	304	134	148	44	46	44	40	127 (7.5)
29		19	49	58	367	308	333	163	179	44	46	44	32	144 (7.6)
30		19	21	33	362	311	333	159	176	44	46	44	34	144 (7.6)

M1: ChemDraw.[2] M2: EPISuite.[3] M3: Satou (1992).[4] M4: Prugh (1973).[5] M5: Butler (1956).[6] M6: Lloyd (1980).[7] M7: Mott (1940).[8] M8: Boie (1953).[9] M9: Kessler (2017).[10] M10: Das (2018).[11] Note: Representative cyclic hydrocarbons were included from ketone cross-condensation reactions due to the large number of possible molecules.
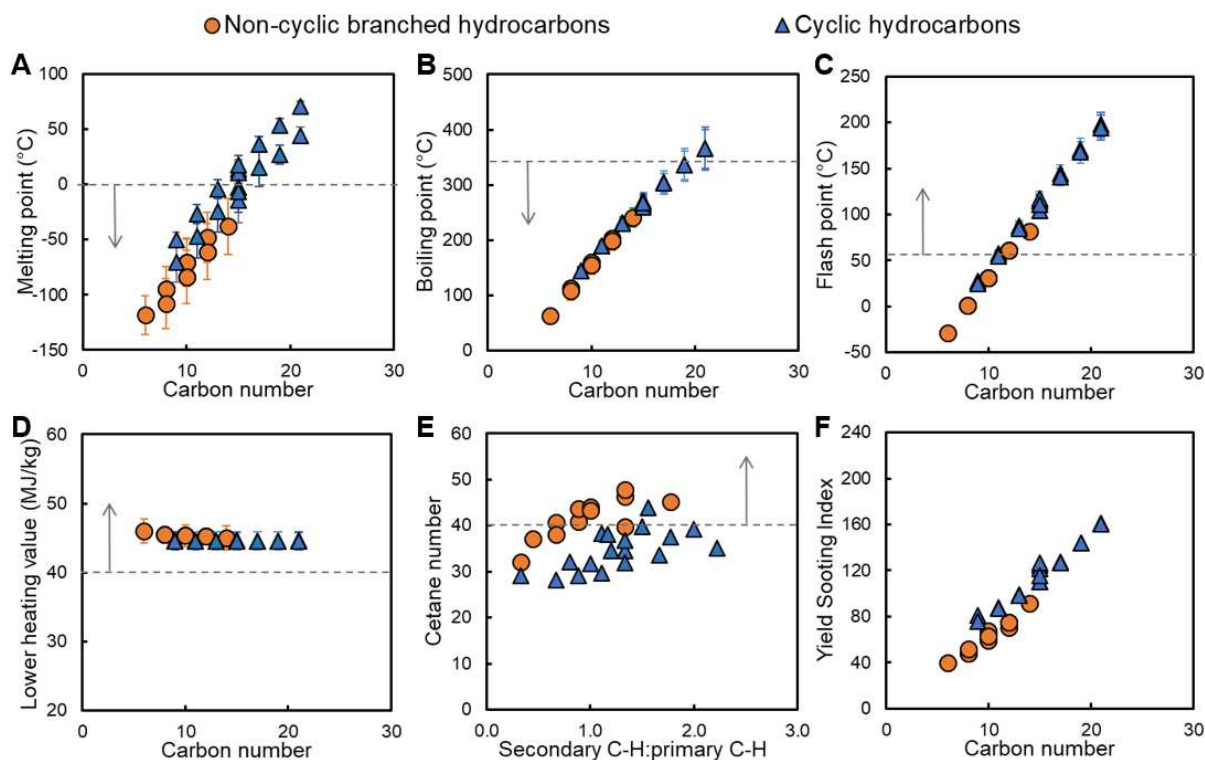
Figure E.1 Plot of model predictions of (A) melting point, (B) boiling point, (C) flash point, (D) lower heating value, (E) cetane number, and (F) yield sooting index. Error bars represent standard deviations of multiple model predictions summarized in Table E.1. Grey dash lines and arrows represent screening criteria.

Table E.2 Surface area, acidity and metal dispersion of fresh ZrO_2, Nb_2O_5, and Pt/Al_2O_3.

Catalyst	Surface area ($m^2 g^{-1}$)	Total acid sites ($\mu mol\ g^{-1}$)	Brønsted acid sites ($\mu mol\ g^{-1}$)	Lewis acid sites ($\mu mol\ g^{-1}$)	Metal dispersion
ZrO_2	65	163	22	141	NA
Nb_2O_5	137	255	49	206	NA
Pt/Al_2O_3	198	329	27	302	9.4%

NA = Not applicable
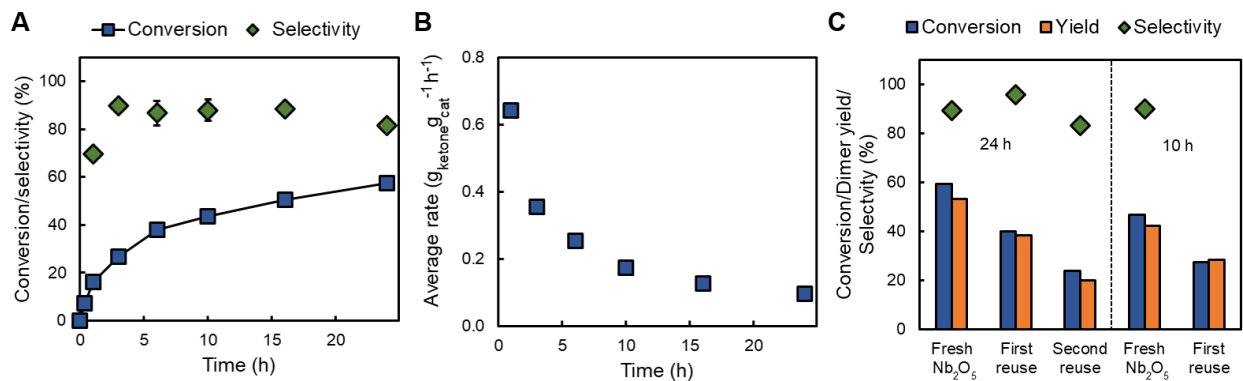
Figure E.2 (A) Conversion of commercial 4-heptanone and selectivity to dimer with reaction time (15 g feed, 20 wt.% 4-heptanone in toluene, 0.75 g fresh Nb_2O_5, catalyst-to-ketone mass ratio = 1:4, 180 °C). (B) Decreasing average rate for 4-heptanone condensation with reaction time (same reaction as figure A). (C) Performance of recycled catalyst (15 g feed, 20 wt% 4-heptanone in toluene, 0.75 g spent catalyst after washing with solvent and drying at room temperature, catalyst-to-ketone mass ratio = 1:4, 180 °C, 10 h or 24 h). All experiments were conducted in an initial He headspace at atmospheric pressure.

Table E.3 Carbon content, surface area and total acidity of fresh Nb_2O_5 and regenerated Nb_2O_5 in Figure 6.4.

Catalyst	C content (wt.%)	Surface area ($m^2 g^{-1}$)	Total acid sites ($\mu mol\ g^{-1}$)
Fresh Nb_2O_5	0	137	255
Regenerated Nb_2O_5 after 1 use	<0.1	123	266
Regenerated Nb_2O_5 after 4 uses	0.3	120	247
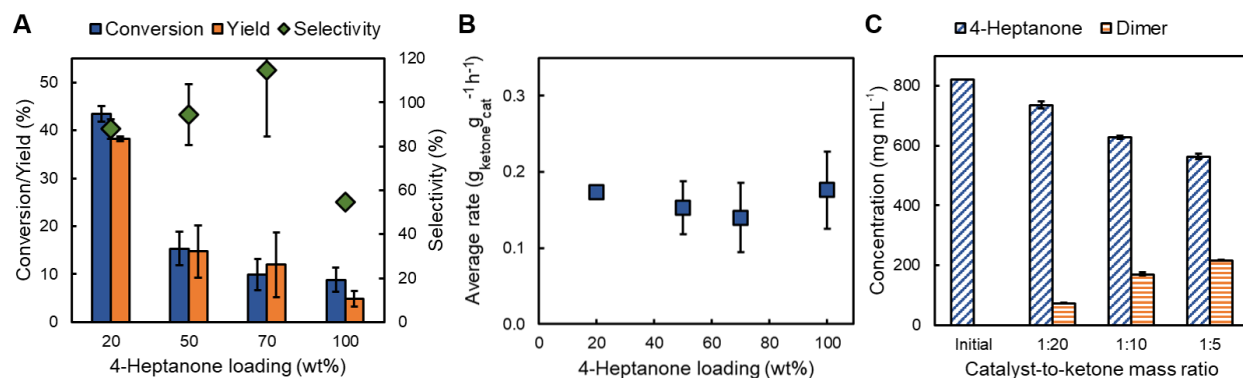
Figure E.3 (A) 4-Heptanone condensation at varying ketone loadings (15 g feed, 0.75 g fresh Nb_2O_5, 20−100 wt% 4-heptanone in toluene, corresponding catalyst-to-ketone mass ratio from 1:4 to 1:20, 180 °C, 10h). (B) Average rate for 4-heptanone condensation (same reaction as figure A). (C) 4-Heptanone and dimer concentrations in the organic phase product at varying fresh Nb_2O_5 loadings (15 g feed, neat 4-heptanone, catalyst-to-ketone mass ratio from 1:20 to 1:5,

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180 °C, 24 h). All experiments were conducted in an initial He headspace at atmospheric pressure.
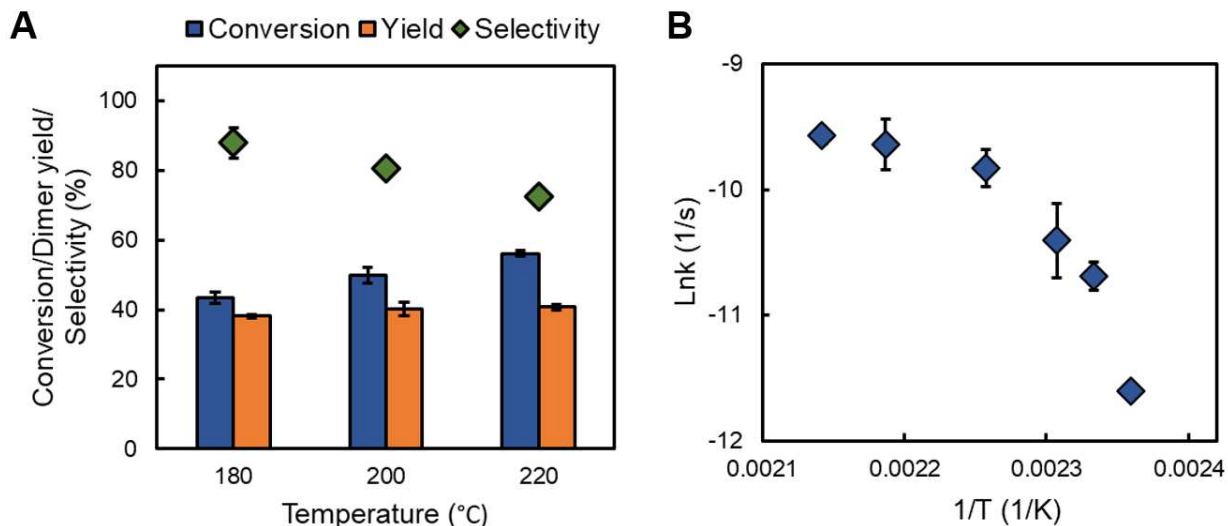
Figure E.4 (A) Conversion of 4-heptanone at varying temperatures (15 g feed, 20 wt% 4-heptanone in toluene, 0.75 g fresh Nb_2O_5, catalyst-to-ketone mass ratio = 1:4, 10 h). (B) Arrhenius plot for 4-heptanone condensation. All experiments were conducted in an initial He headspace at atmospheric pressure.
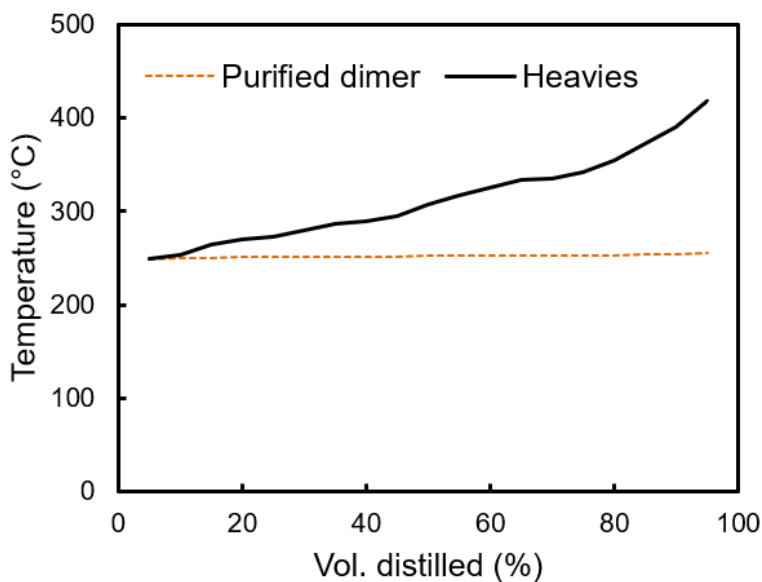
Figure E.5 Simulated distillation curves of purified dimer and heavier compounds (heavies were obtained from removing dimer by distillation).
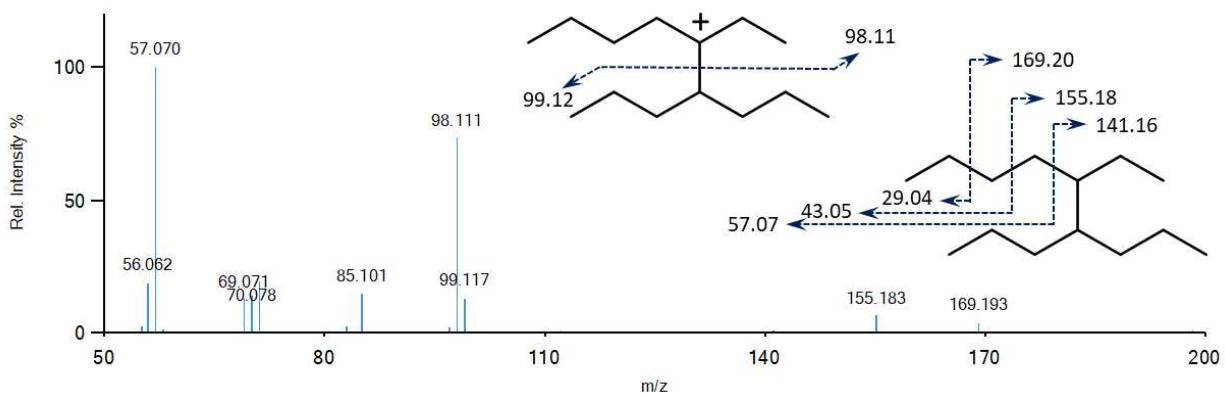
Figure E.6 High resolution mass spectra of the C$_{14}$ hydrocarbon.
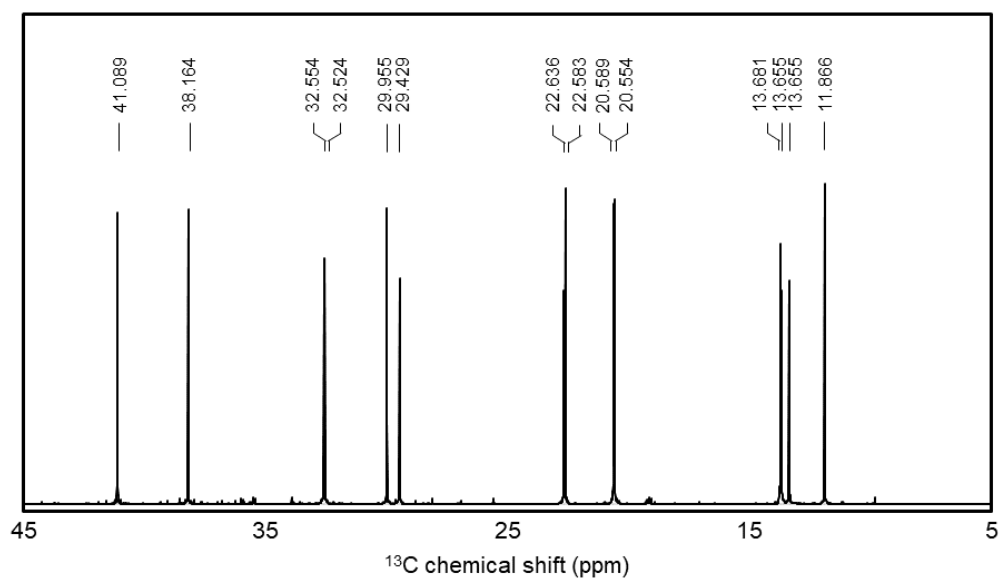
Figure E.7 ^{13}C NMR spectrum of purified C$_{14}$ hydrocarbon.

Table E.4 Physicochemical properties of fresh and regenerated Pt/Al$_2$O$_3$.

Catalyst	Pt content (wt.%)	Metal dispersion	Surface area (m^2 g^{-1})	Total acid sites (µmol g^{-1})
Fresh	3.34	9.4%	198	1054
Regenerated	3.36	9.3%	197	1044
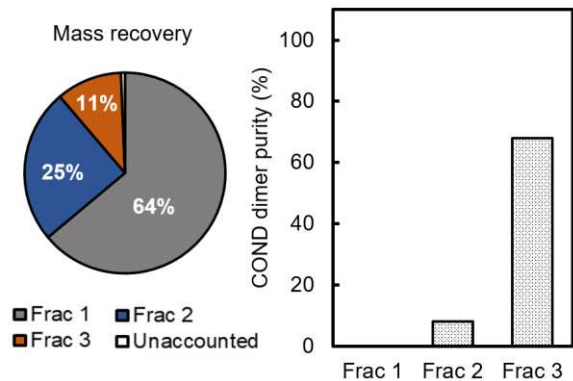
Figure E.8 Mass recovery and dimer purity in three distillation fractions when distilling condensation product.
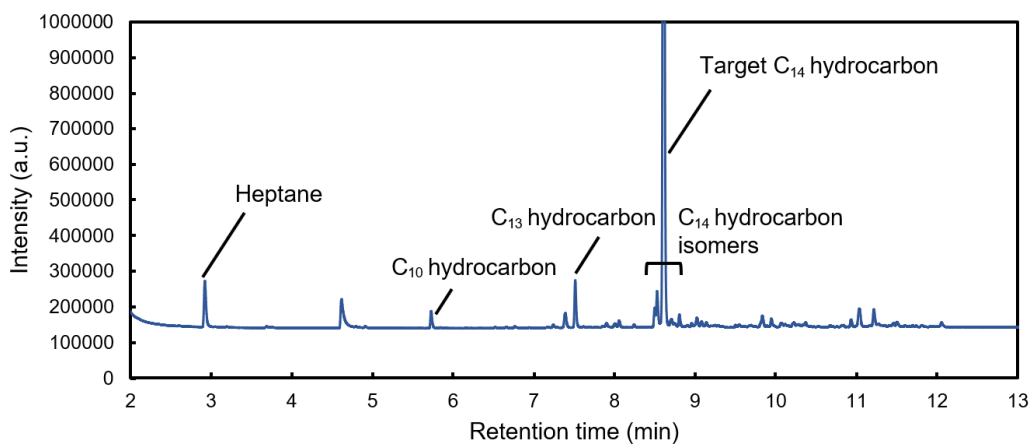
Figure E.9 GC-Polyarc/FID chromatogram of crude hydrocarbon blendstock from upgrading commercial butyric acid. The major component is the target non-cyclic branched C_{14} hydrocarbon. Scale was adjusted to highlight minor components. Peak at 4.6 min was from solvent impurity.
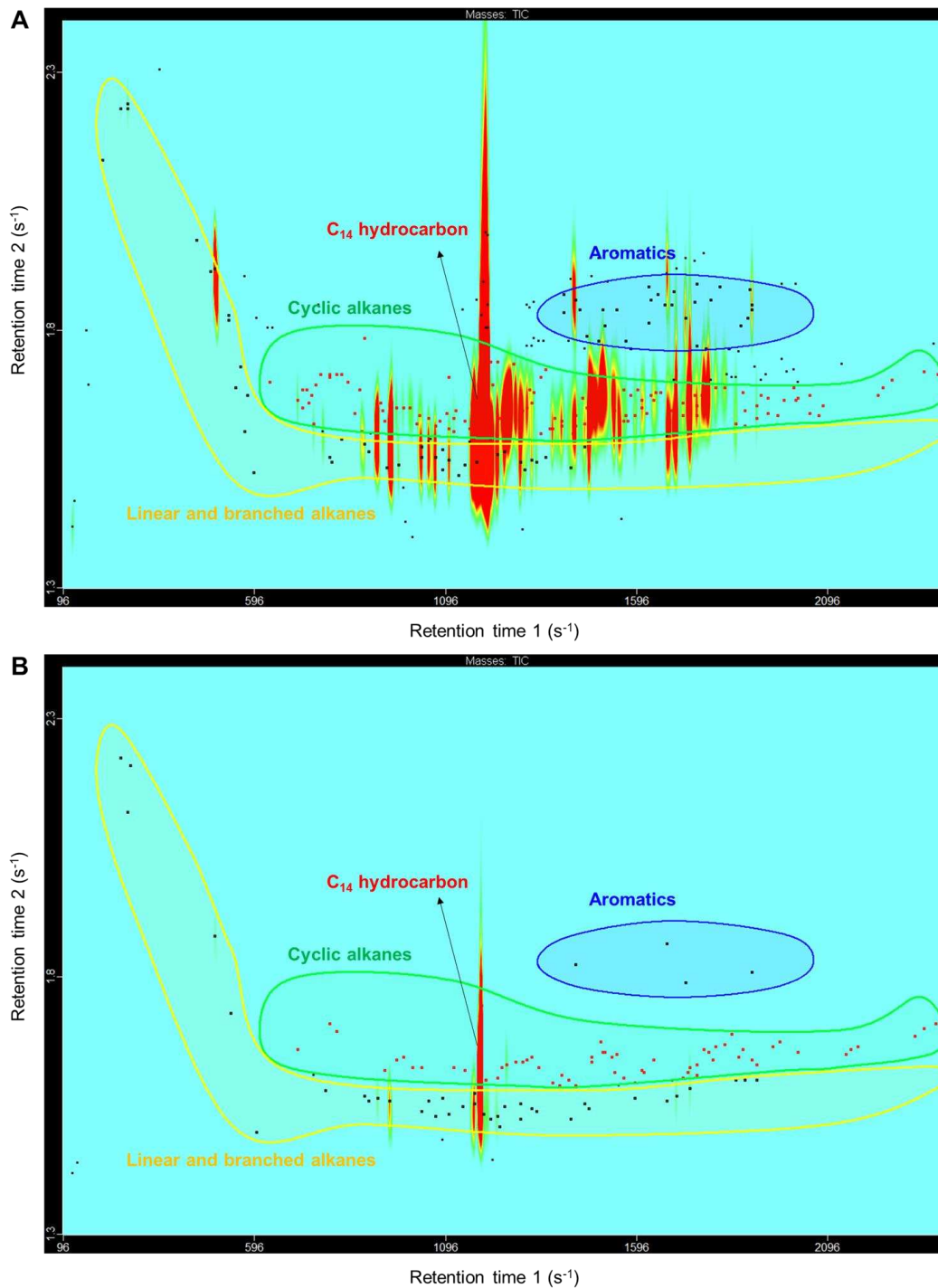
Figure E.10 GC×GC-TOFMS chromatogram of crude hydrocarbon blendstock from upgrading commercial butyric acid: (a) dilution 20:1 and (b) dilution 400:1. The major component is the target non-cyclic C_{14} hydrocarbon. The most abundant classes present in the mixture are non-cyclic alkanes and cyclic alkanes, although there is potential overlap between these classes and ambiguous identification of linear alkanes and alkenes in these regions. Other structures identified in the plot include aromatics. Note that results are not quantitative.

	Crude C$_{14}$		Pure C$_{14}$	
No. of H attached	Carbon ratio (%)	No. of H attached	Carbon ratio (%)	
0	1.5	0	0	
1	15.1	1	14.3	
2	55.6	2	57.1	
3	27.8	3	28.6	
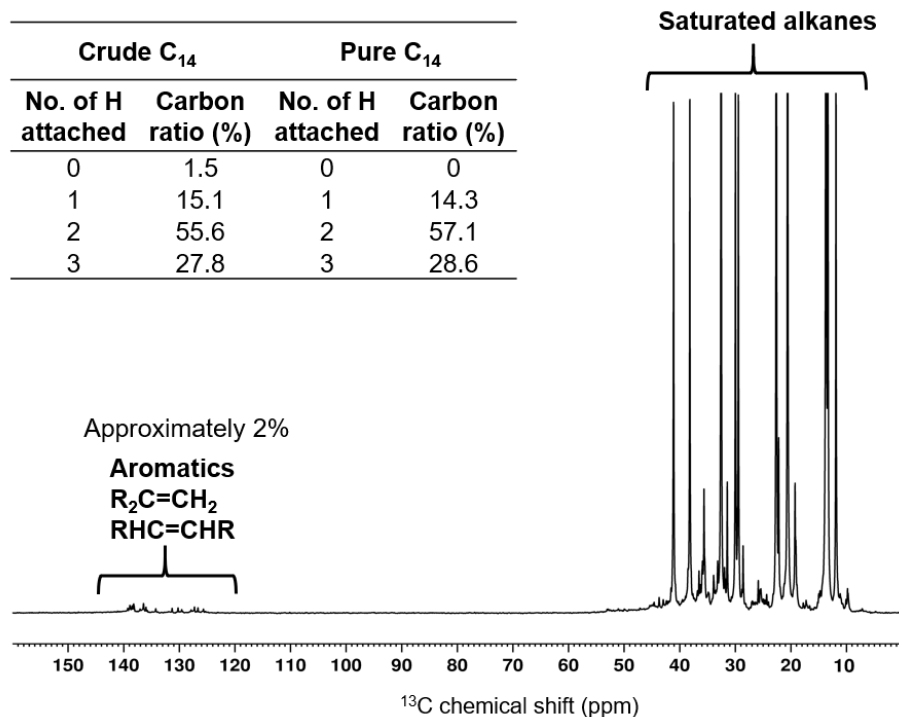
Figure E.11 ^{13}C NMR analysis of crude hydrocarbon blendstock from upgrading commercial butyric acid. The crude blendstock exhibited approximately 2% carbon in double bond or aromatic bond. Compared with pure C$_{14}$ hydrocarbon, the crude blendstock displayed 3% decrease in the ratio of primary carbon. The ratio of carbon having two hydrogen attached (mostly secondary carbon) also decreased 3%. Accordingly, the ratio of carbon having one or no hydrogen attached (e.g., tertiary carbon, quaternary carbon, aromatic carbon) slightly increased.

Table E.5 Concentrations of monomeric and total sugars in concentrated deacetylated dilute acid enzyme hydrolysate. Total sugars account for soluble oligomeric sugars.

Concentration (g L^{-1})	Sucrose	Glucose	Xylose	Galactose	Arabinose	Fructose
Monomeric sugar	29.15	253.52	136.47	8.09	20.29	5.62
Total sugar	ND	292.80	149.29	8.46	19.96	1.35

ND = Not determined.
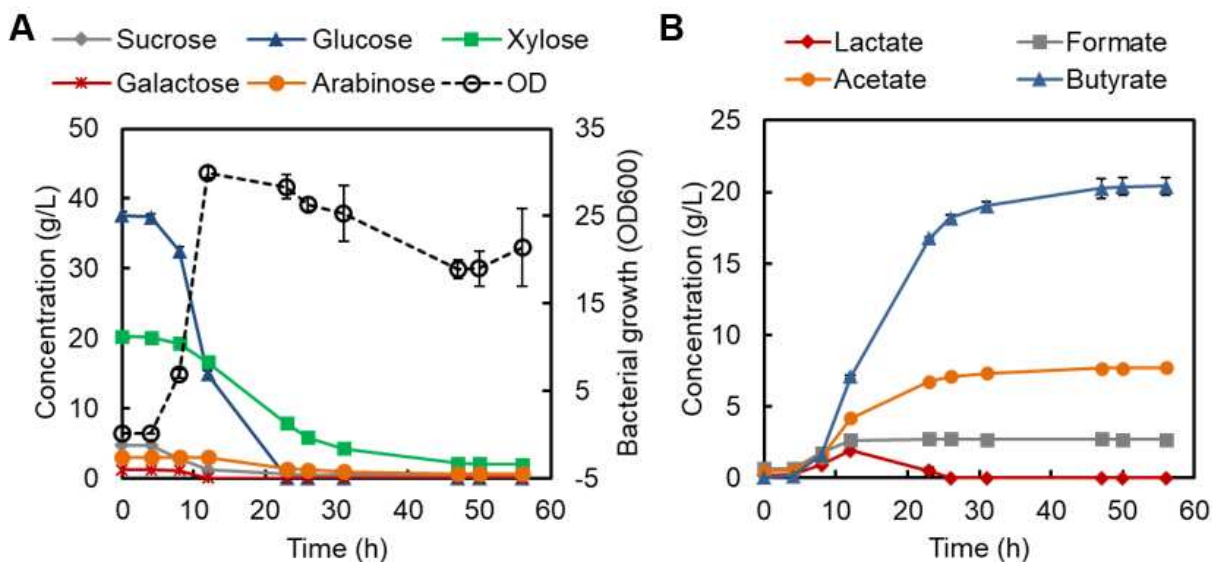
Figure E.12 Batch conversion of lignocellulosic sugars by *Clostridium butyricum* (ATCC 19398). (A) Sugar utilization and bacterial growth measured as optical density at 600 nm (OD). (B) Butyric acid and byproducts formation. Data show the average of two biological replicates. Error bars represent the absolute difference between those replicates.

Table E.6 Impurities in the acid feed and organic phase products from upgrading of biologically derived butyric acid

Element concentration ($\mu g\ g^{-1}$)[a]	N[b]	S	Si	Ca	Na	P	K	B	Al	Fe	Ti	Mg
Bio-butyric acid feed	<2	<5	<100	<5	24	<1	<20	<5	<1	1	<0.1	<1
Ketonization product	<2	<5	160	<5	<10	<1	<20	<5	<1	<1	<0.1	<1
Condensation product	<2	<5	340	<5	<10	<1	<20	<5	1	<1	<0.1	<1
HDO product[c]	<2	<5	<100	<5	<10	<1	<20	<5	<1	<1	<0.1	<1

[a]Data obtained with ICP-AES.
[b]Data obtained with chemiluminescence, unit is mg L^{-1}.
[c]Before removing cyclohexane solvent.

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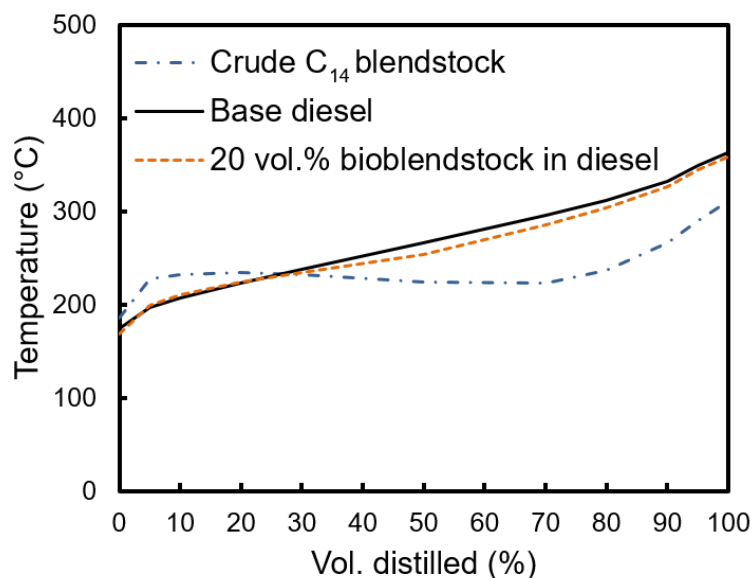
Figure E.13 Simulated distillation curves of commercial butyric acid derived crude C_{14} blendstock, base diesel, and diesel blend with 20 vol% bioblendstock (D86 correlation was applied to all three curves).
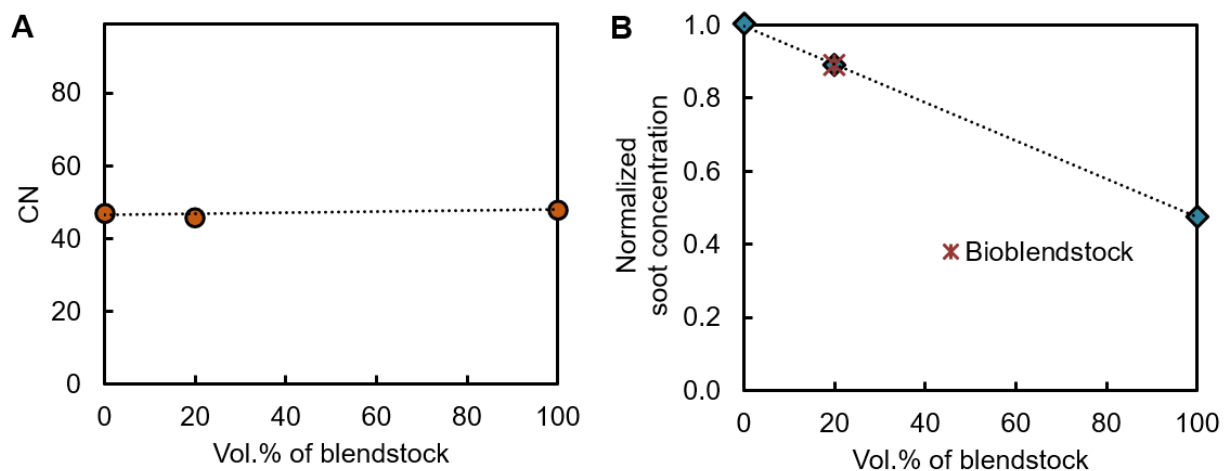
Figure E.14 Pot of (A) CN and (B) normalized soot concentration over blend ratio of commercial butyric acid derived crude C_{14} blendstock (and bioblendstock as indicated in figure). Dotted lines are to guide the eye.

E.3   References
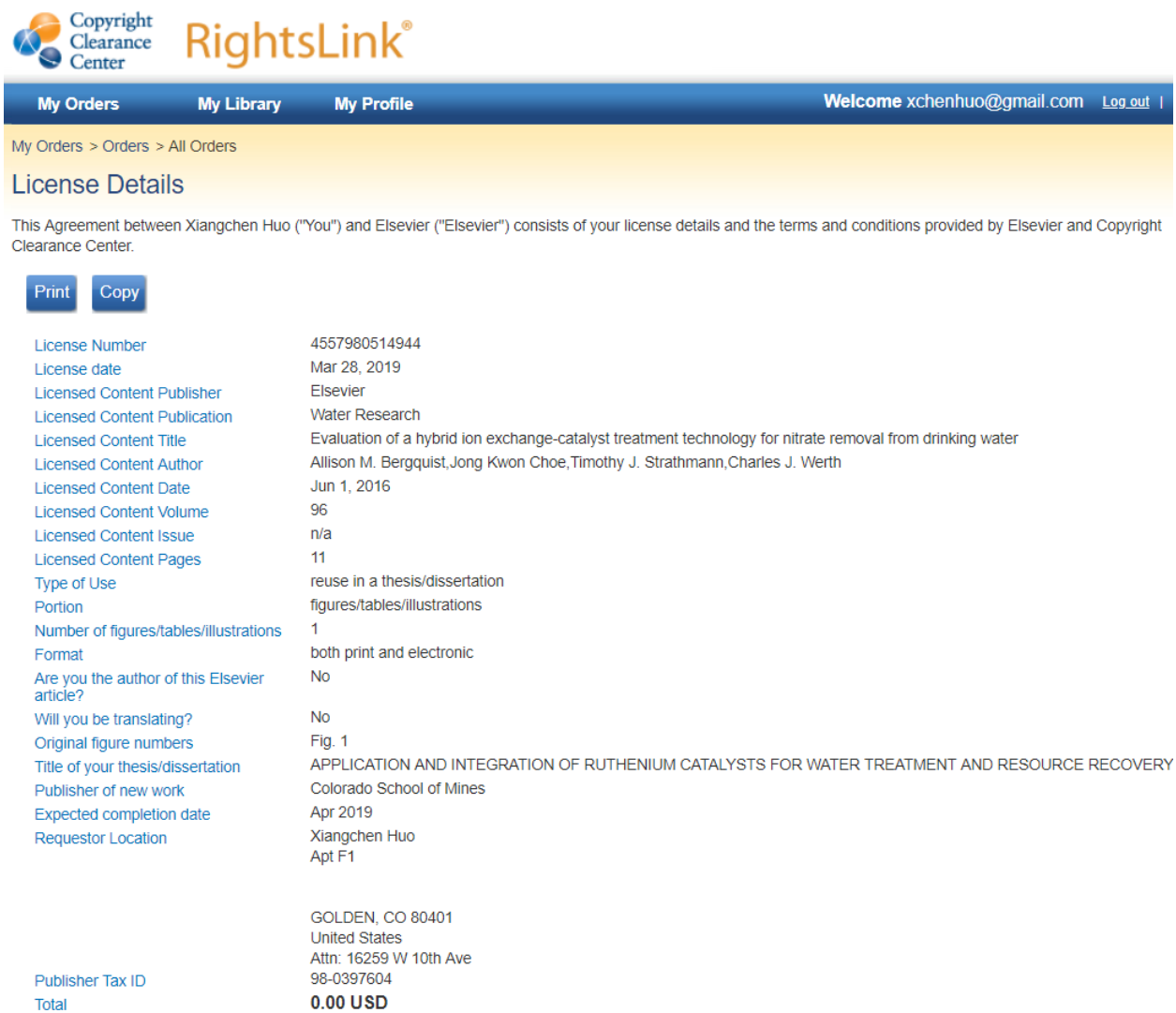
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APPENDIX F

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From: Hunter Mack
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Hunter

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