GOLD NANOSTRUCTURES
SUPPORTED ON METAL OXIDES
AND THEIR APPLICATION AS
CATALYSTS

by

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This thesis responds to a body of work performed and defended at both Jacobs University Bremen and Colorado school of Mines, and is regarded as the fulfillment of a joint Ph.d program between the two institutions.
ABSTRACT

Gold has long been considered an ‘inert’ metal. However, catalysis by gold has rapidly become a hot topic in chemistry after the discovery that nano-scale gold is highly active for CO oxidation even at room temperature which is not possible by other metals. The applications of gold catalysts have been extended to hydrogenation, epoxidation, alcohols and aldehydes oxidation, and even aerobic oxidation of alkanes. Several mechanisms have been proposed mainly based on the study of CO oxidation, but the nature of the active Au species/structure/site remains obscure.

In this work, by designing several gold catalysts and comparing their activities in the aerobic oxidation of benzyl alcohol, I found the crystal facet structure of the MgO support has a significant impact on the activities of gold nanoparticles and the Au-support interface can influence the thermal stability of gold nanoparticles and thus their activities at high temperature. My experimental results support the proposal that: the electronic effects of the Au-support interface strongly influences the catalytic activity. The electronic effect can be enhanced by increasing the contact interface or choosing electron rich supports such as those with highly polar surfaces or rich in vacancies.

I also realized in my Ph.d research that gold/metal oxide is a complex catalysis system. The nature of metal oxides, the crystal facet of metal oxides, the vacancies on metal oxides, the surface area of metal oxides, the interface between gold and metal oxides, the shape and size of gold nanoparticles all play important roles. Even I tried my best to keep other factors identical when study on one factor, the influence from other factors cannot be absolutely excluded from the results. That is a common problem faced...
by all research groups. However, that is also the reason why gold/metal oxides catalysts can attract so much attention from scientists from all over the world.
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CHAPTER 1 INTRODUCTION

1.1 Gold nanomaterials

An atom measures about 1 ångström, or $10^{-10}$ meters. The study of atoms and molecules is the conventional field of chemistry as was studied in the late 19th and 20th centuries. A nanometer (nm), or $10^{-9}$ meters, represents a collection of a few atoms or molecules. Properties of bulk substances of micrometer sizes or larger have been studied for years by solid state physicists and material scientists and are generally reasonably well understood. It was just recently shown that on 1–100 nm scale the properties of a material become dependent on its size and shape. However, the interface between substances is just now beginning to be understood. New properties develop on the nanoscale due to the lack of symmetry at the interface or to electron confinement that do not scale linearly with size. Thus, the nanometer scale (1–100 nm) incorporates collections of atoms or molecules, whose properties are neither those of the individual constituents nor those of the bulk. On this scale, many of the atoms are still located on the surface, or one layer removed from the surface, as opposed to the interior. New properties are observed on this scale due to the interface that is not observed in the bulk or individual atoms. Since the properties depend on the size of the structure, instead of the nature of the material, reliable and continual change can be achieved using a single material.

Gold nanoparticles is one of the materials have long been known to generate beautifully colored glass by adding gold to generate burgundy, reds, or purples [1]. Faraday attributed this color to very finely divided colloidal gold, or gold nanoparticles as
known today. As the size or shape of the nanoparticle changes, the observed color also changes. Gold spheres have a characteristic red color, while silver spheres are yellow. More recent treatments have shown that the color is due to the collective oscillation of the electrons in the conduction band, known as the surface plasmon oscillation or surface plasmon resonance. The oscillation frequency is usually in the visible region for gold and silver giving rise to the strong surface plasmon resonance absorption. Therefore, the origins of properties on the nanoscale are different for metal nanoparticles than for semiconductor nanoparticles.

Nanorods with tunable aspect ratio have great potential to show unique optical [2, 3], magnetic, electronic and chemical properties based on their anisotropic structure. Nanorods also have enhanced emission over bulk metal and nanospheres, due to the large enhancement of the longitudinal plasmon resonance [4-7]. Clusters [8] and nanorods [6, 7] have an emission that shifts wavelengths as the size or aspect ratio increases, respectively. For nanorods, the longitudinal plasmon resonance enhances the radiative cross section of the interband transition of bulk gold leading to shifting emission wavelengths and intensities depending on the overlap between the two transitions [6, 7]. The observed emission of gold nanorods is reported [7] with quantum yields of $10^{-4}$–$10^{-5}$. The emission wavelength increases as the aspect ratio of the nanorod is increased. Several synthetic methods exist for preparing metallic nanorods, including electrochemical deposition [9] in hard templates [10], photochemical synthesis [11] and seed-mediated growth [12, 13]. Gold nanorods with controllable aspect ratios from 2 to 25 have been prepared by seed-mediated growth procedures [12-14]. Recent mechanistic and kinetic studies have shown that the final structure of the gold nanorods was determined by the crystal structure of the
gold seeds [15] and that the nanorod growth rate decelerated throughout the initial growth phase [16]. The seed-mediated growth procedure can also be adapted to grow gold nanorods directly on flat solid surfaces by using seeds immobilized on the surface [17, 18]. The seed particles were believed to first grow to a minimum diameter of 17 nm before nanorod formation is initiated on solid surface [19].

The channels in mesoporous materials, typically with diameters of 2-30 nm, are a class of promising templates to synthesize nanostructured materials [20-22] by controlling the pore size and structure [23, 24] using different templates [25] and synthesis procedures [26, 27]. Gold nanowires have been obtained in the channels of mesoporous SBA-15 by hydrogen flow reduction [28, 29] and electroless reduction [30]. Due to the well-defined ordered porous structure of SBA-15, gold nanowires formed in the channels of SBA-15 have a uniform diameter which is normally smaller than that of the nanorods prepared by typical seed-mediated methods, especially for the case of high aspect ratio nanorods. However, the length of those gold nanowires are not well defined because the narrow channels in SBA-15, a few nanometers in diameter and several micrometers in length, are not an efficient mass transfer system [31], which makes the choice of reducing agent an important factor for the synthesis of gold nanostructures within the matrix. Both the high-temperature hydrogen flow [28] and the hydroxylamine used in electroless reduction [30] are relatively strong reducing agents. A fast reduction of the gold precursor in an inefficient mass transfer system may result in an irregular growth of the nanorods. However, it is necessary to control the size of gold nanorods to get 3D-gold nanorods in a solid matrix. Both theoretical calculation [32] and experimental results [33] showed the 2D periodic arrays of nanorods are high-quality
polarizers due to the interactions between nanorods, multipole contributions and formations of photonic gaps. Therefore, it is quite reasonable to expect some interesting applications as optical polarizers from the well-ordered 3D gold nanorods in porous materials as compared with 2D nanorod arrays on flat solid surface.

1.2 Gold and silver nanocatalysts

Catalytic performances of nanoparticles can be finely tuned either by their composition, which mediates electronic structure, or by their shape, which determines surface atomic arrangement and coordination. Beyond the exciting potential for tailoring catalysts, nanostructured materials introduce additional challenges to catalyst design. Being small and with surface atoms of different unsaturated valencies, nanoparticles of specific shape are more liable to change their shape in the harsh medium of chemical reactions. That raises concerns about durability, what the true active species is, and approaches to control this phenomenon. Surface reconstruction and/or dissolution of active atoms on corners or edges by one or more of the reactants or even the solvent is an additional concern that requires attention. Despite these challenges, several types of chemical reactions that have been catalyzed using transition metal nanomaterials include cross couplings, electron transfers, hydrogenations, fuel cell electrocatalysis and oxidations.

The Group 11 metals have a long history for their uses in jewelry, ornaments and as ‘coinage metals’ as well being particularly interesting on the nanoscale for the colors they display as a function of size. However, as research has progressed with regard to size (and shape) related chemical reactivities, the rich chemistry of this group of metals is
emerging and particularly their application as catalysts. Gold in its bulk state has long been thought to be far less catalytically active than other transition metals, such as Ag, Pt, and Pd. Recently, researchers [34-36] have reported some pioneering works to indicate that gold could catalyze hydrogenation, hydrogen exchange, hydrocracking, and carbon monoxide oxidation reactions. These initial findings have inspired numerous investigations into the nature of ultrafine gold particles dispersed on supports using various approaches [37, 38].

For many years, the chemistry of silver and gold was believed to be similar. Silver is the best conductor among metals and so silver nanoparticles facilitate more electron transfer than gold nanoparticles. Silver has a reduction potential of +0.79 V versus normal hydrogen electrode (NHE) for Ag\(^+\) (aqueous)/Ag\(_{metal}\) system. But for Ag\(^+\) (aqueous)/Ag\(_{atom}\) system, it is −1.80 V versus NHE. Among the many different metal nanoparticles under investigation, silver nanoparticles are emerging as one of the most intensively studied because of the broad range of applications exhibited. These properties include shape and size dependent optical, electronic, and chemical properties, and thus present many possibilities with respect to technological applications.

1.2.1 Preparation of gold catalysts

There are two general paradigms for the preparation of nanoscale materials, “top down” and “bottom up”. Those preparations characterized by breaking down larger starting materials are classified as “top down” while those consisting of building up from atomic or molecular starting materials are “bottom up”. Chemical reduction methods such as alcohol reduction [39-41] hydrogen reduction [42-44], sodium borohydride reduction [45-47], etc. have been the most common methods of synthesizing colloidal
metal nanoparticles. Other reduction methods such as electrochemical [48, 49], photochemical [50-52], and sonochemical reduction methods [53, 54] have also been used to a smaller extent. Many different stabilizers have been used as capping agents for the synthesis of colloidal metal nanocatalysts such as polymers [55, 56], dendrimers [57, 58], block copolymer micelles [56, 59], surfactants [60, 61], etc. Supported metal nanocatalysts have been prepared by the adsorption of the colloidal metal nanocatalysts onto the support [62-64], grafting of the nanoparticles onto the support [65], etc. Supported metal nanocatalysts can also be lithographically fabricated using electron beam lithography [66, 67]. Numerous review references have been published on the use of colloidal and supported transition metal nanoparticles as catalysts for a variety of organic and inorganic reactions.

Beyond the preparation of nanoscale materials in the form of colloids, there are considerable efforts placed on the preparation of supported heterogeneous catalysts, in particular the nature of the support and the process to immobilize active metal on the support (mostly metal oxides and active carbon).

Due to the lower melting point and poor affinity for metal oxides, it is difficult to prepare stable gold catalysts well dispersed on metal oxides. The impregnation methods which are widely used to prepare supported Pd or Pt catalysts do not work well in the case of gold because the presence of the chloride ion can significantly enhance the coagulation of gold particles during the calcination of HAuCl₄.

Haruta summarized the methods to prepare supported gold catalyst and categorized them into four groups [68]. The first group (Table 1-1) includes co-
precipitation [69], amorphous alloying [70] and co-sputtering [71]. These procedures generally consist of two steps: the preparation of well-mixed gold/metal oxide precursors; and the transformation of gold precursor into gold particles normally by calcinations in air above 550K. Well mixed precursors and high temperature calcination are both important to make a strong contact between Au particles the crystalline metal oxides.

The strategy of the second approach is based on the concept to deposit or adsorb Au compounds on metal oxide surfaces (Table 1-1). Amongst the three methods mentioned in this group, the deposition and precipitation (DP) method is widely used for producing active Au catalysts. By controlling the pH and the concentration of the HAuCl₄ solution, the deposition of Au(OH)₃ can be controlled on the surfaces of the support metal oxides to prevent the precipitation in the liquid phase. The aggregation of gold nanoparticles induced by chloride ions can be prevented by washing the gold compound before drying, which is one of the reasons for the high activity of these catalysts. The primary limitation is that DP can only be applied to the metal oxides with isoelectron potentials (IEPs) above 5. For example, Au(OH)₃ cannot be deposited on SiO₂ and active carbon. However, some recent studies showed this constraint can be overcome by proper surface modification [72].

The procedure of the third group (Table 1-1) is to directly immobilize Au colloids on modified metal oxide surfaces. In theory, this method can be applied to every metal oxide and the catalysts prepared by this method normally have a good gold particle size distribution but often suffer from relatively poor contact between gold particles and the support.
Table 1-1 Preparation Techniques for Nanoparticulate Gold Catalysts.

<table>
<thead>
<tr>
<th>Categories</th>
<th>Preparation techniques</th>
<th>Support materials</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation of mixed precursors of Au and the metal component of supports</td>
<td>Co-precipitation (hydroxides or carbonates) CP</td>
<td>Be(OH)₂, TiO₂, Mn₂O₃, Fe₂O₃, Co₃O₄, NiO, ZnO, In₂O₃, SnO₂</td>
<td>[69, 76, 77]</td>
</tr>
<tr>
<td></td>
<td>amorphous alloy (metals) AA</td>
<td>ZrO₂</td>
<td>[70]</td>
</tr>
<tr>
<td></td>
<td>co-sputtering (oxides) in the presence of O₂</td>
<td>Co₃O₄</td>
<td>[71]</td>
</tr>
<tr>
<td>Strong interaction of Au precursors with support materials</td>
<td>deposition-precipitation (HAuCl₄ in aqueous solution) DP</td>
<td>Mg(OH)₂, Al₂O₃, TiO₂, Fe₂O₃, Co₃O₄, NiO, ZnO, ZrO₂, CeO₂, Ti-SiO₂</td>
<td>[78]</td>
</tr>
<tr>
<td></td>
<td>liquid phase grafting (organogold complex in organic solvents) LG</td>
<td>TiO₂, MnOₓ, Fe₂O₃</td>
<td>[79, 80]</td>
</tr>
<tr>
<td></td>
<td>gas phase grafting (organogold complex) GG</td>
<td>all kinds, including SiO₂, Al₂O₃-SiO₂, and activated carbon</td>
<td>[81, 82]</td>
</tr>
<tr>
<td>Mixing colloidal Au with support materials</td>
<td>colloid mixing CM</td>
<td>TiO₂, activated carbon</td>
<td>[38]</td>
</tr>
<tr>
<td>Model catalysts using single crystal supports</td>
<td>vacuum deposition VD (at low temperature)</td>
<td>Defects are the sites for deposition, MgO, SiO₂, TiO₂</td>
<td>[73-75]</td>
</tr>
</tbody>
</table>

The vacuum deposition is a most important method to prepare model catalysts which play a critical role in studying the mechanism especially the active sites of supported gold catalysts. Au anion clusters can be deposited with homogeneous dispersion at relatively low temperatures [73, 74] on single crystals of MgO and TiO₂.
rutile). Surface defects or specific surface cages are suggested as sites for stabilizing the Au clusters [73, 75].

1.2.2 Selective oxidation of CO

In the 1980s Haruta group found that gold nanoparticles supported on α-Fe₂O₃ were highly active in the oxidation of CO (Figure 1-1) especially at very low temperatures [83]. This surprisingly high activity is not replicated by other metals. In their later work, Au/TiO₂ was found to be an equally effective catalyst [76]. After this, gold nanocatalysts supported on different metal oxides were thoroughly studied.

Owing to the possible applications of polymer electrolyte fuel cells to automobiles and to residential electricity-heat delivery systems, low-temperature water-gas-shift reaction is attracting renewed interests. In comparison with commercial catalysts based on Ni or Cu, which are operated at 900K or at 600 K, respectively, supported Au catalysts appear to be advantageous in operation at a temperature as low as 473 K [84]. During the course of investigation on the hydrogenation of CO₂ over supported Au catalysts, it was found that Au/TiO₂ was selective to the formation of CO, namely, reverse water-gas-shift reaction at a temperature as low as 473K [84]. Later, Au/TiO₂ was confirmed to be active for water-gas-shift reaction [85]. Andreeva and coworkers were the first to apply Au catalysts to water-gas-shift reaction and reported that Au/Fe₂O₃ and Au/ZrO₂ were most active.

The oxidation of CO is a typical reaction for which Au catalysts are extraordinarily active at room temperature and much more active than the other noble metal catalysts at temperatures below 400 K. One of the foci of recent work is the
mechanism for CO oxidation [86, 87]. Although the literature in this area is vast and sometimes contradictory, there are several pieces of information that are critical to developing an understanding of the mechanism. Active catalysts always contain metallic Au particles which give a CO absorption band at 2112 cm$^{-1}$, while oxidic Au species which give a CO absorption band at 2151 cm$^{-1}$ are not responsible for steady-state high catalytic activity [88]. However, smooth surfaces of metallic Au do not adsorb CO at room temperature [89], indicating that CO is adsorbed only on steps, edges, and corner sites. Thus, smaller metallic Au particles are preferable [90].

![Figure 1-1 CO conversion over various catalysts as a function of temperature. 1) Au/α-Fe$_2$O$_3$ (Au/Fe=1/19, co-precipitation, 400 °C), 2) 0.5 wt % Pd/Y-Al$_2$O$_3$ (impregnation, 300 °C), 3) fine Au powder, 4) Co$_3$O$_4$ (carbonate, 400 °C), 5) NiO (hydrate, 200 °C), 6) α-Fe$_2$O$_3$ (hydrate, 400 °C), 7) 5 wt % Au/α-Fe$_2$O$_3$ (impregnation, 200 °C), and 8) 5 wt % Au/Y-Al$_2$O$_3$ (impregnation, 200 °C).](image-url)

A theoretical calculation [91] has explained why the smooth surface of Au is noble in the dissociative adsorption of hydrogen. However, when Au is deposited as nanoparticles on metal oxides by means of co-precipitation and deposition–precipitation techniques, it exhibits surprisingly high catalytic activity for CO oxidation at a
temperature as low as 200K [37, 76]. This finding has motivated many scientists and engineers to investigate the Au catalysis in 1990s.

One of the remarkable works among those studies was done by Corma and co-workers who reported that gold nanoparticles supported on nanocrystalline CeO$_2$ using DP method were very active catalysts for CO oxidation (Figure 1-2). These catalysts have been found to be an order of magnitude more active than comparable catalysts prepared using a non-nanocrystalline support for CO oxidation. Au/CeO$_2$ catalyst also shows excellent selectivity for CO oxidation in the presence of H$_2$ at 60°C (the temperature close to the operation temperature of fuel cell) where selectivity of normal Au active catalysts will be negatively affected [92].

Most of the reported gold catalysts active in CO oxidation are prepared by the DP method which gives catalysts a strong interaction between gold and the metal oxides matrix. But one main constraint of this method is it can not be used to deposit gold at metal oxides with IEPs(isoelectric point)<5, such as SiO$_2$. Sheng Dai [72] and co-
workers successfully deposited gold at the surface of mesoporous SiO$_2$ by the DP method after a sol-gel surface modification with TiO$_2$. The results show the gold nanoparticles (0.8-1.0 nm) in the mesopores (Figure 1-3) are highly active for CO oxidation.

![Figure 1-3 The scheme to prepare gold/mesoporous material catalysts (left) and Z-contrast TEM image of ultrasmall gold nanoparticles on ordered mesoporous materials. The bright spots (0.8-1.0 nm) correspond to gold nanoparticles.](image)

It is now widely recognized that the supported gold nanocatalysts are highly active in the low-temperature oxidation of CO. However, many questions remain concerning the relatively simple reaction of CO oxidation. For example, what is the reaction mechanism and what is the nature of the active site?

A substantial part of the reported research on CO oxidation catalyzed by supported gold was motivated by the goal of identifying catalyst properties that affect the activity. Two early classes of observations were important in determining the approaches used recently to investigate supported gold catalysts: (a) various preparation routes lead to catalysts with different activities [76, 94], and (b) catalysts consisting of gold supported on reducible metal oxides (e.g., Fe$_2$O$_3$, CeO$_2$, and TiO$_2$) are typically more active than those supported on non-reducible metal oxides (e.g., $\gamma$-Al$_2$O$_3$, MgO, and
SiO$_2$). Such observations led to wide acceptance of the inferences that the preparation method influences activity [37] and that the support plays a role in the catalysis.

![Figure 1-4](image)

**Figure 1-4** Representation of an active site and possible reaction mechanism for CO oxidation catalyzed by supported gold.

Bond and Thompson [94], in their review of the literature up to 2000, proposed a mechanism for CO oxidation catalyzed by supported gold that was an attempt to reconcile some apparently contradictory hypotheses (Scheme 1). Their proposed active site consists of nanoparticles incorporating both zero valent and cationic gold, the latter positioned at the metal–support interface. Their suggestion of the presence of cationic gold was based on observations by various authors of vCO infrared IR bands characteristic of CO bonded to cationic gold, but they lacked evidence of such species in working catalysts and of their suggestion that cationic gold was a “glue” holding the nanoclusters to the support.

Haruta [95] presented a review in 2002 and proposed, on the basis of measurements of the kinetics of CO oxidation catalyzed by supported gold, that there are
three temperature regions, with different kinetics and activation energies of the CO oxidation reaction. He suggested that at temperatures below 200 K, the reaction catalyzed by Au/TiO\(_2\) takes place at the surfaces of small gold nanoparticles dispersed on the support, but at temperatures above 300 K, the reaction occurs at gold atoms at the perimeter sites of the supported gold nanoparticles.

However, silver catalysts also have a relatively high activity for CO selective oxidation at low temperatures. A silver catalyst is deactivated remarkably after pretreatment in H\(_2\) at high temperatures, whereas treatment in oxygen at high temperatures could reactivate the catalyst. Interestingly, the changes in activities are mostly reversible. The structures of the silver particles experience massive changes during the course of various pretreatments and the existence of subsurface oxygen resulting from an oxygen treatment at high temperatures is crucial for high selectivity and activity in CO selective oxidation [96, 97]. Since CO oxidation is generally claimed to be a structure-sensitive reaction, the restructuring of silver particles is likely to exert an influence on the activity of the catalyst. Yang and Aoyama [98, 99] have studied the thermal stability of uniform silver clusters supported on oxidized silicon or aluminum surfaces in both oxidizing and reducing atmospheres and found the thermal stability of the silver clusters was significantly lowered in an oxidizing condition and that heating above 350 °C in an oxidizing condition can induce a migration of the silver clusters.

Size selectivity in catalysis was reported for the propylene partial oxidation and the low-temperature CO oxidation where Ag nanoparticles smaller than about 5 nm in diameter were shown to be as active as the Au nanoparticles. For the ethylene epoxidation, only Ag particles larger than about 30 nm can catalyze the reaction [100].
Most of the focus has been on the use of spherical or undetermined shaped nanoparticles to catalyze reactions. There are very few studies in which catalysis is conducted with nanoparticles of known shapes \cite{101}, e.g. using truncated octahedral Pt nanoparticles to catalyze the electron-transfer reaction and using cubic Pt nanoparticles for the decomposition of the oxalate capping agent. Formation of different oxygen species depending on the Ag particle size sputtered on the highly ordered pyrolytic graphite (HOPG) surface, resulting in variation in catalytic activity of CO oxidation using oxygen under ultra high vacuum (UHV) conditions revealed CO oxidation is sensitive towards the size of particle \cite{102}. The oxygen uptake of a smaller Ag nanoparticle is significantly higher than that of a larger particle and bulk-like Ag enhancing the reactivity of CO oxidation.

Recent progress in polymer electrolyte membrane fuel cells has particularly motivated the search for a highly efficient catalyst for the CO selective oxidation at low temperature. Thus, combinations of metals in the forms of alloys, core/shell and ‘decorated’ surfaces (Pt, Pd, Rh, Ru, Au, Ag, Cu, Co, Fe, In, Ga) with different supports—zeolite, Al$_2$O$_3$, SiO$_2$, and activated carbon have produced active catalysts for the CO reaction. One such alternative catalyst, gold–silver alloy nanoparticles deposited on MCM-41 demonstrated exceptionally high catalytic activity, comparable to the most active catalysts, such as Au/TiO$_2$ and Au/Fe$_2$O$_3$ \cite{103, 104}. The alloying of Au and Ag shows a strong synergistic effect in promoting the low-temperature oxidation of CO \cite{105}. The alloy catalyst activation depends on the composition (Ag ratio is crucial), aluminum content in the support and pretreatment conditions.
1.2.3 Epoxidation reactions

Since Hayashi found that Au supported on TiO$_2$ could catalyze the epoxidation of propylene in the gas phase containing O$_2$ and H$_2$, the catalytic properties of Au/TiO$_2$ and related systems have attracted the interest of chemical industries as well as academia. Propylene oxide (PO) is one of the world’s most important bulk chemicals, which is used for producing polyurethane and polyols. Current industrial processes utilize two-staged chemical reactions using either Cl$_2$ or organic peroxides yielding byproducts stoichiometrically.

From both an environmental and an economic point of view, the direct synthesis of PO by the use of molecular oxygen has long been a big academic challenge. Supported noble metal catalysts such as Ag/carbonates and/or titanates, Pd/TS-1, Pd–Pt/TS-1 [106-108], and Au/TiO$_2$ [109, 110] are reported to be active in this process.

In 1998, Haruta and co-workers found nanoscale gold catalysts, prepared by the DP technique (which showed a high activity in the CO oxidation due to the strong contact with the support at highly dispersed isolated tetrahedral Ti$^{4+}$ sites) could also provide very high PO selectivity (>99%) in a gas phase containing O$_2$ and H$_2$ under ambient pressure. They also found the formation of PO over Au-based catalysts is a typical structure-sensitive reaction [110]. Only hemispherical Au particles (Figure 1-5) with a suitable size (2 nm<dAu(diameter of gold nanoparticles)<10 nm) will selectively produce PO. In their recent work, organically modified mesoporous titanosilicate was also proven to be an efficient support [111] which gives reasonably efficient H$_2$ consumption, high yields, and PO selectivities(>90%) [112].
Their studies initiated growing research interests both from industries and from academia [113-116]. One of the more remarkable studies was done by Hutchings and co-workers [115]. They used catalytic amounts of peroxides to initiate the oxidation of alkenes with O$_2$ and make it unnecessary to sacrifice H$_2$ to activate O$_2$. Au/graphite was found to be very active to catalyze the expoxidation of cyclohexene, styrene, cis-stilbene, and cyclooctene even in a solvent free system. Though the selectivity can be increased by using the proper solvent, for example toluene, the environment-friendly expoxidation in
solvent-free systems are more attractive to chemical industry and certainly will become another hot research topic.

Silver is considered almost a uniquely effective catalyst for the heterogeneous epoxidation reaction. The mechanism of the epoxidation of ethylene with oxygen over silver catalyst has been largely studied [117-119]. In spite of numerous studies of this catalytic system and although it is widely used, some questions remain unanswered: how supports and promoters affect the reaction, what the mechanism of primary and secondary reactions is, and what relationship exits between the electron and structure factors. The interaction of oxygen with metal surfaces has been suggested to be one of the most important elementary steps in heterogeneous catalysis. Reviews for oxygen adsorption, active oxygen species, promoter effects and reaction mechanism on the silver catalysts have frequently been reported [120]. Oxygen species on silver were found to play a key role in ethylene epoxidation and extensive work has been performed to establish the interaction of oxygen with silver surfaces. i.e. chemisorbed atomic oxygen or chemisorbed molecular oxygen [121]. Surface molecular, surface atomic, subsurface atomic, and bulk atomic oxygen species have been reported in the literature.

Significant efforts to improve the selectivity include the use of different silver precursors, use of different preparation techniques, and the use of promoters is gained simply by the continuous addition of a chlorine-containing hydrocarbon species to the gaseous reactants as a moderator, which also acts to depress overall reaction rates. Campbell reported that small amount of promoters like Cl increased the ethylene oxide selectivity [122, 123]. In an industrial oxidation of ethylene, alkali metal ions are an important additive for a silver catalyst. Alkali or alkaline earth promoters, such as cesium,
provide another substantial improvement [119, 124, 125]. Campbell [124] reported the role of a cesium promoter in silver catalysts for the selective oxidation of ethylene. Oxidation of ethylene in solution catalyzed by polymer-protected silver colloids and on the promotion effect by alkali metal ions on colloidal silver catalysts also has been studied [126]. Colloidal dispersions of silver nanoclusters protected by the poly(sodium acrylate) increased the rate of oxidation with increase of reaction temperature in catalytic activity with the addition of Cs(I) and Re(VII) ions [127].

The effect of silver particle size on the reaction rate is a well known property of supported silver catalysts [128, 129]. The study on distribution of the Ag supported on alumina and reported that the silver particles of 30–70Å on alumina or silica showed higher activities. It has been shown that the small silver clusters more effectively, most probably, due to electronics and other properties of silver (atom environment, electron work function, electric conductance, etc.) differ considerably from those of the bulk silver. The majority of studies have used bulk silver samples, and there is still uncertainty as to the nature of the active sites for ethylene epoxidation on the commercial catalyst. It has been found that enlargement of the silver particles decreases the amount of subsurface oxygen and results in the appearance of nucleophilic oxygen. These results have been used for discussion of a possible explanation of the size effect in ethylene epoxidation over Ag/Al2O3 catalysts [130, 131]. The kinetic study and shape controlled epoxidation of olefins catalytic activity of these nanoparticles on several supports such as α-Al2O3, CaCO3 and spherical particles of TiO2 obtained by the Stöber method was investigated in the epoxidation of a non-allylic olefin such as styrene, as well as for an allylic olefin, such as propene, using molecular oxygen and N2O as oxidants.
Silver supported on titania was found to be active for propene epoxidation using hydrogen/oxygen mixtures at 50 °C [132, 133]. Direct aerobic epoxidation of alkenes catalyzed by silver nanoparticle stabilized by the H₃PV₂Mo₄₀O₁₄₀ polyoxometalate supported on α-Al₂O₃ in molecular oxygen were capable of epoxidation in liquid phase [134]. Styrene is a useful alkene model to study the mechanism reaction of terminal alkene epoxidation. The size and morphology of silver nanoparticles affect the catalytic behavior of silver catalysts supported on α-Al₂O₃ and MgO in the selective oxidation of styrene in gas phase [135-139]. Epoxidation of styrene to styrene oxide by molecular oxygen was studied using the Cs loaded silver nanowire catalysts resulted in desired product with greater selectivity.

1.2.4 Selective Oxidation of hydrocarbons

The selective oxidation of alkanes with molecular oxygen is a challenging problem [140, 141]. The production of more valuable oxidized products in relation to the low-cost raw materials is economically interesting. The chemical inertness of hydrocarbons makes the activation of C-H bonds particularly difficult, usually requiring dramatic reaction conditions, such as high temperature and pressure. Cyclohexane oxidation is of special interest industrially, because this process produces an important KA-oil (a mixture of cyclohexanone and cyclohexanol) intermediate in the petroleum industrial chemistry. Such oil can be used for the production of adipic acid and -caprolactam, which are key materials for manufacturing 6,6-nylon and 6-nylon [142] respectively. Modern industrial methods usually require high pressure and temperature when using soluble cobalt as the catalyst, which leads to the realization of high selectivity for the sum of cyclohexanone and cyclohexanol only at a low conversion, since the
products, cyclohexanone and cyclohexanol, are substantially more reactive than the cyclohexane reactant. It is difficult to receive high conversion and selectivity simultaneously under mild conditions.

It is desirable to find a good catalyst to activate the reaction between oxygen and cyclohexane. However, the technology with which cyclohexane is oxidized by O\(_2\) to produce cyclohexanone and cyclohexanol has not been improved to date [143]. In the effort to cut down the use of environmentally harmful elements, heterogeneous catalysts prepared by immobilizing Mn\(^{III}\), Co\(^{III}\), Cr\(^{III}\) and Fe\(^{III}\) ions on metal oxides were developed for the oxidation of cyclohexane [144-146]. However, these systems were found to suffer from leaching under the reaction conditions used. Mesoporous materials were reported as efficient support materials because cyclohexane is more readily oxidized than cyclohexanol in the pores and therefore the selectivity is enhanced.

Zhao and co-workers applied gold nanoparticles for this application. They reported that supported gold catalysts can activate cyclohexane at 150 °C with selectivities around 90 % [147, 148]. Under similar reaction conditions, Kake Zhu and co-workers found that gold nanoparticles immobilized in the channels of SBA-15 by different methods had a good performance in catalyzing the aerobic oxidation of cyclohexane in solvent free system [149]. The highest conversion was reported as 32%. In order to enhance selectivity, the aerobic oxidation of cyclohexane was performed under 100 °C catalyzed by supported Au, Pt and Pd catalysts [150]. The selectivity for cylohexanone and cyclohexanol was found to decline rapidly with enhanced conversion and longer reaction times. The gold catalysts were found to give identical performance to the Pt and Pd catalysts.
Silver catalysts have also found use in hydrocarbon oxidation reactions. Since the first patent on the manufacture of ethylene oxide with an Ag catalyst by Lefort in 1931 [151], the industrial production of ethylene oxide by direct oxidation in gas phase has become a widely used process largely converted into ethylene glycol or a variety of other derivatives. Selective oxidation of ethylene to ethylene oxide over supported material in the gas phase is not only one of the very few uses of that element as a catalyst of industrial importance but also of fundamental interests in surface science and the subject has been extensively reviewed [152].

Silver has rarely been considered as a catalyst for selective oxidation of saturated hydrocarbons. Nanoscale silver supported on the MCM-41 for the liquid phase oxidation of cyclohexane was found to be effective catalyst in the absence of solvent [153]. The higher turn over number and improved selectivity in comparison to other support systems of Ag/TS-1 and Ag/Al₂O₃ was observed.
1.2.5 Oxidation of alcohols and aldehydes

Alcohol and polyols oxidation are also important processes in industrial chemistry and it is not surprising that there is a significant effort to improve upon current technologies and particularly to make the processes more "green". The objective of this research has been the development of a catalytic system that could be competitive to a stoichiometric approach involving strong and toxic oxidizing agents. Supported platinum and palladium catalysts are well known as effective catalysts for the oxidation of polyols in acidic or basic condition. However, supported gold nanoparticles were also found to be very effective in the oxidation of alcohols, including diols in the presence of base [154-161]. These catalysts can also be used in the oxidation of sugars, glucose and sorbitol [162, 163]. By using dioxygen as the oxidant, Carrettin group reported a 100 % selectivity in the oxidation of glycerol to glycerate catalyzed by Au catalysts supported on graphite under relatively mild conditions, with yields approaching 60 % [164-166]. In their work, the presence of base was also found to be essential for both activity and selectivity.

It is a common observation that the oxidation of alcohols catalyzed by supported gold catalysts have better performances in basic conditions towards obtaining high selectivities and reasonable activities though the mechanism behind this chemistry is still unclear. Another interesting observation is that the type of supports of gold catalysts, which show an important role in the oxidation of CO and epoxidation, seem to have little effect in the oxidation of alcohols. Rossi and co-workers even found unsupported colloidal gold particles are as active as Au nanoparticles supported on active carbon under the same conditions in the oxidation of glucose to gluconic acid. Subsequent study
extended the application of colloidal gold catalysts to the oxidation of 1,2-diols [167, 168]. The disadvantage of unsupported colloidal gold catalysts is the poor long-term performance compared with the supported gold nanocatalysts because of the aggregation. Recently, gold nanoclusters stabilized by polymers [169] showed good activity in the aerobic oxidation of benzyl alcohol in aqueous media.

Figure 1-7 (A) Benzyl alcohol conversion and selectivity in benzaldehyde with the reaction time at 373 K and 0.1 MPa pO2. Squares, Au/TiO2; circles, Pd/TiO2; and triangles, Au-Pd/TiO2. Solid symbols indicate conversion, and open symbols indicate selectivity. (B) Au-Pd/TiO2 catalyzed reactions at 363 K, 0.1 MPa pO2, for cinnamyl alcohol (squares) and vanillyl alcohol (circles). Solid symbols indicate conversion, and open symbols indicate selectivity to the corresponding aldehydes.

However, Corma and co-workers [170, 171] proposed that the support of Au/CeO2 catalysts can help to stabilize a reactive peroxo intermediate from O2 and therefore can enhance the activities of gold catalysts in the selective oxidation of alcohols to aldehydes/ketones and the oxidation of aldehydes to acids. One further interesting point in their reports is that the gold catalysts work well in the solvent free system.
without any additional base thus making this work considerably different from earlier research.

One of the most significant advances in the field of alcohol oxidation has come from the Hutchings research group which showed that Au/Pt alloy supported on TiO$_2$ was a highly active catalyst for the oxidation of benzyl alcohol, cinnamyl alcohol and vanillyl alcohol. In particular, for the oxidation of benzyl alcohol, the performance of the Au-Pd/TiO$_2$ catalyst is remarkably better than the that of Au/TiO$_2$ and Pd/TiO$_2$ in term of both conversion and selectivity (Figure 1-7) [172].

The silver-catalyzed partial oxidation of methanol to formaldehyde, industrially important chemical transformation of alcohols to carbonyls in the gas phase, significant in the synthesis of drugs, vitamins, fragrances and many complex synthesis was first employed on an industrial scale by BASF AG in 1905. Since that time several silver-based catalysts, including bulk and supported systems, have been developed for the oxidation of alcohols. Low catalytic activity at low temperature or the products of cracking and/or overoxidation at a higher reaction temperature are mainly the encountered problems with bulk silver. Attempts have been made to improve the catalytic performance of silver-based catalysts by either adding additives to bulk silver catalysts or dispersing the silver particles on supports [173-176]. Supported silver is expected to enhance the dispersion and stability of silver, and thus also enhance its catalytic activity at relatively low temperatures. The design of a catalyst combining the advantages of both the bulk silver catalysts (conventional electrolytic silver) and the supported silver catalysts with better performance remains a challenge for research on alcohol catalytic oxidation [177].
Supported platinum and palladium nanoparticles are generally acknowledged as effective catalysts for the oxidation of polyols [178]. In situ electrolytic nano-silver/zeolite film/copper grid catalyst have shown higher catalytic oxidation properties towards mono, di, and other types of alcohols with higher selectivity. The silver nanoparticles generated in-situ, highly dispersed on the zeolite film and precoated on a copper grid demonstrated excellent activity towards polyhydric alcohol at low temperature. The performance effectively avoids the problems of both over-oxidation and C–C bond cracking at a high temperature or the mild oxidation at a low temperature as in the case of the practical electrolytic silver catalyst. Au-Ag alloy clusters (size range 1.6-2.2 nm) with various Ag contents (5-30%) prepared by the co-reduction method in the presence of poly(N-vinyl-2-pyrrolidone) have been investigated for aerobic oxidation of p-hydroxybenzyl alcohol as a model reaction to understand the effect of Ag on the catalytic activity of Au clusters. Rate constants per unit surface area for Au-Ag:PVP clusters with small Ag content (<10%) were larger than those of monometallic Au:PVP clusters of comparable size. Spherical nanoparticles anchored on the external walls of multiwalled carbon nanotubes, Ag/MWNT composite electrode exhibited a high catalytic activity for the electro-oxidation of methanol.

**1.2.6 Direct synthesis of hydrogen peroxide**

As mentioned above, recently there has been great interest in the design of new heterogeneous catalysts for selective oxidation under ambient conditions, and these typically use hydrogen peroxide as the oxidant [108]. At present, hydrogen peroxide is produced by the sequential hydrogenation and oxidation of alkyl anthraquinone and global production is ca. $1.9 \times 10^6$ tons per year. However, there are problems associated
with the anthraquinone route, including the cost of the quinone solvent system and the requirement for the periodic replacement of anthraquinone because of hydrogenation. In view of this, there is considerable interest in the direct manufacture of hydrogen peroxide from the catalyzed reaction of hydrogen and oxygen. At present, some success has been achieved using Pd as a catalyst, especially when halides are used as promoters. Typically, dilute solutions of hydrogen peroxide are produced, and earlier studies indicated that the Pd catalyst can be combined with an oxidation catalyst, TS-1, so that the hydrogen peroxide produced is used in situ. However, no commercial process exists for the direct manufacture of hydrogen peroxide. Hutchings and co-workers were the first to show that Au/Al₂O₃ catalysts were effective for the direct reaction. Thus far, the best catalysts found are Pt-Au alloy supported catalysts which showed better performance than pure Pd or Au catalysts [179, 180]. It was believed that the enhanced activity observed by the addition of Pd to Au was due to the enhanced activation of hydrogen, but if too much Pd was added the decomposition activity of the hydrogen peroxide was also enhanced and so the rate declined.

Subsequently, Ishihara group [181] have shown that Au/SiO₂ and Au-Pd/SiO₂ catalysts are also effective for this reaction at only 10 °C. In recent studies, Hutchings and co-workers have shown that the selectivity for H₂ utilization can be significantly enhanced when Fe₂O₃ and TiO₂ are used as supports[182, 183].Indeed, at short reaction times the selectivity can be greater than 95 % for the reaction of dilute H₂/O₂ mixtures (1:1, 5 vol %) diluted with CO₂ (95 vol %). Very high rates of reaction were observed with noncalcined Au-Pd/TiO₂ catalysts, but these catalysts were unstable, losing both Au and Pd during the reaction, and they could not be successfully reused. However, if the
catalysts are calcined at 400 °C prior to use very stable reusable catalysts are obtained. Detailed structural investigation of these active stable catalysts using XPS and TEM showed that the catalysts have a core-shell structure with a gold-rich core and a palladium-rich shell. It was concluded that the Au was acting as an electronic promoter for the Pd-rich surface of the Au-Pd nanocrystals.

Table 1-2 Formation of H₂O₂ from the reaction of H₂/O₂ over Au and Pd catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent a</th>
<th>Temperature °C</th>
<th>Pressure MPa</th>
<th>O₂/H₂ mol ratio</th>
<th>H₂O₂ mmol g(catalyst)⁻¹ h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/Al₂O₃</td>
<td>CH₃OH</td>
<td>2</td>
<td>3.7</td>
<td>1.2</td>
<td>1530</td>
</tr>
<tr>
<td>Au : Pd (1:1)/Al₂O₃</td>
<td>CH₃OH</td>
<td>2</td>
<td>3.7</td>
<td>1.2</td>
<td>4460</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>CH₃OH</td>
<td>2</td>
<td>3.7</td>
<td>1.2</td>
<td>370</td>
</tr>
<tr>
<td>Au/ZnO</td>
<td>SCCO₂</td>
<td>35</td>
<td>9.2</td>
<td>1.0</td>
<td>9</td>
</tr>
<tr>
<td>Au : Pd (1:3)/ZnO</td>
<td>SCCO₂</td>
<td>35</td>
<td>9.2</td>
<td>1.1</td>
<td>7</td>
</tr>
<tr>
<td>Au : Pd (1:1)/ZnO</td>
<td>SCCO₂</td>
<td>35</td>
<td>9.2</td>
<td>0.8</td>
<td>12</td>
</tr>
<tr>
<td>Au : Pd (3:1)/ZnO</td>
<td>SCCO₂</td>
<td>35</td>
<td>9.2</td>
<td>0.9</td>
<td>8</td>
</tr>
<tr>
<td>Pd/ZnO</td>
<td>SCCO₂</td>
<td>35</td>
<td>9.2</td>
<td>1.3</td>
<td>0</td>
</tr>
</tbody>
</table>

* SCCO₂ = supercritical CO₂

1.2.7 The Future of Gold Nanocatalysts

Gold catalysts with selected support materials can also promote many reactions other than CO oxidation.

Table 1-3 lists such reactions, which usually take place at much lower temperatures or with much higher degrees of selectivity over Au catalysts than over other metal catalysts [184]. The characteristic features of supported gold catalysts are remarkable structure sensitivity of their catalytic performance, low apparent activation
energies (active at low temperatures), and moisture activation. By taking advantages of these properties, R & D efforts on Au catalysts are expected to expand in three directions.

**Table 1-3 Ongoing and potential applications of Au catalysts.**

<table>
<thead>
<tr>
<th>Fields of applications</th>
<th>Reactants or Reactions</th>
<th>Support materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indoor air quality control</td>
<td>odour (commercialized), CO, sick house gases</td>
<td>Fe$_2$O$_3$, TiO$_2$</td>
</tr>
<tr>
<td>Pollutant abatement</td>
<td>dioxin oxidation-ecomposition, NO reduction, N2O decomposition</td>
<td>Fe$_2$O$_3$, Al$_2$O$_3$, Co$_3$O$_4$</td>
</tr>
<tr>
<td>H2 energy carrier</td>
<td>water-gas shift, CO removal, fuel cell anode</td>
<td>ZrO$_2$, CeO$_2$, Al$_2$O$_3$, Mn$_2$O$_3$, Fe$_3$O$_5$, carbon black</td>
</tr>
<tr>
<td>Chemical process</td>
<td>Hydrochlorination, hydrogenation, liquid-phase selective oxidation, propylene epoxidation</td>
<td>AuCl$_3$/activated carbon, ZnO, activated carbon, TiO$_2$(anatase), Ti-SiO$_2$</td>
</tr>
</tbody>
</table>

The first direction involves the discovery of new capabilities for Au particles larger than 2 nm that are stable up to 673K. Combinations with other metal catalysts might contribute to further develop the capabilities of Au catalysts.

The second direction involves application of the mechanism of Au catalysis and the techniques developed for preparing Au catalysts to other noble metals. In most cases, the genesis of the catalysis of Au is ascribed to the perimeter interfaces around the Au particles. This presents us with a new guiding principle for creating a wide range of new catalytic systems, because the combination of catalytic metals with a variety of support materials should present numerous novel catalysts.
1.3 Supported material for gold catalysts

The availability of efficient gold catalysts was the driving force of many researches devoted to the analysis of the different factors controlling the activity. Unfortunately, despite numerous studies published on supported gold catalysts, there is still no clear picture with respect to the origin of the catalytic activity, and often, the results reported in the literature concerning gold catalysis are contradictory. The role of the support is still under discussion. The fact is the activity of gold catalysts highly depends on the supporting materials.

But in general, high-surface porous materials are good candidates for supporting materials. In the reaction catalyzed by supported metal nanocatalysts, reaction takes place at the surface of supported materials where metal nanoparticles are immobilized. The large surface area is one of the key characteristic for support materials to give good catalyst activity.

1.3.1 High surface area Aerogel

Aerogels, dried gels with a very high relative pore volume, are one type of promising materials that might be as the host for metal nanocatalysts. These are versatile materials that are synthesized in a first step by low-temperature traditional sol-gel chemistry (Figure 1-8). However, while in the final step most wet gels are often dried by evaporation to produce so-called xerogels, aerogels are dried by other techniques, essentially supercritical drying. All materials that can be synthesized as wet gels by the sol-gel process can then be dried by the supercritical method to obtain aerogels.
As a result, the dry samples keep the very unusual porous texture which they had in the wet stage. In general these dry solids have very low apparent densities, large specific surface areas, and in most cases they exhibit amorphous structures when examined by X-ray diffraction (XRD) methods. In addition, they are metastable from the point of view of their thermodynamic properties. Consequently, they often undergo structural evolution by chemical transformation, when aged in a liquid medium and/or heat treated. The particularly interesting properties of aerogels arise from the extraordinary flexibility of the sol-gel processing, coupled with original drying techniques, which greatly enhance the facility to dope nanocatalysts on aerogel as support materials. The wet chemistry is not basically different for making xerogels and aerogels. Figure 1-9 shows a typical MgO aerogel reported by Kenneth J. Klabunde.
research group [185]. The MgO aerogel is aggregation of 4nm MgO cubes which show (001) facet under high-resolution TEM. This material has a surface area of 350-400 m$^2$/g.

Figure 1-9 TEM (A) and High-resolution TEM (B) of AP-MgO. Note the cubelike nanocrystals that amalgamate into polyhedral structures with many corners/edges, and the embryonic pore structure.

A remarkable improvement in MgO aerogel is achieved by Richards’ group recently by adding benzyl alcohol in the preparation which helps to guide the growth of MgO crystal and ends up with MgO nanosheets with (111) facet [186]. NiO with (111) facet (Figure 1-11) has also been synthesized by Richards’ group[187].

One of the unique properties of those kind of (111) materials is their high surface energy. The highly polarized (111) facets make them an interesting material as support of gold catalysts given the assumption the interface between gold nanoparticles and supporting materials plays an important role in catalytic activity.
1.3.2 Mesoporous Materials

Porous materials are classified into microporous materials, mesoporous materials and macroporous materials by their size according to IUPAC notation. Microporous
materials have pore diameters of less than 2 nm and macroporous materials have pore diameters of greater than 50 nm; the mesoporous category fall in the middle.

The first mesoporous material, with a long range order was reported by Japanese researchers in 1990. Around that time, the synthesis was also reported by the group of the former Mobil Oil Company [188, 189]. Then, mesoporous oxides of niobium, tantalum, titanium, zirconium, cerium and tin have also been prepared. Mesoporous materials have prospective applications in catalysis, sorption, gas sensing, optics, and photovoltaic. Mesoporous silica is a typical mesoporous material due to the strong affinity between silica precursors and surfactants.

Mesoporous silica has well-defined nano-porous structures that are formed over templates via self-assembly processes. Mesoporous silica materials have huge surface areas, making them ideal for use as catalysts to facilitate chemical reactions. Their uniform nanometer-sized pores allow them to separate molecules by size difference. Their pores may also be used to trap drug molecules for controlled drug release. Therefore, the ability to tailor the pore structure of mesoporous material is of fundamental importance for various chemical and biological applications. There has been tremendous interest about tailoring mesoporous materials with unique pore structures and pore sizes.
Table 1-4 Preparation and physicochemical properties of hexagonal SBA-15 prepared with poly(alkylene oxide) triblock copolymers. The value inside brackets for d(100) is the value for the SBA-15 product calcined at 500°C for 6 hours.

<table>
<thead>
<tr>
<th>Block copolymer</th>
<th>Reaction temperature (°C)</th>
<th>d(100) (Å)</th>
<th>BET surface area (m²/g)</th>
<th>Pore size (Å)</th>
<th>Pore volume (cm³/g)</th>
<th>Wall thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EO₁₂PO₇₀EO₅</td>
<td>35</td>
<td>118 (117)</td>
<td>630</td>
<td>100</td>
<td>1.04</td>
<td>35</td>
</tr>
<tr>
<td>EO₂₀PO₇₀EO₂₀</td>
<td>35</td>
<td>104 (95.7)</td>
<td>690</td>
<td>47</td>
<td>0.56</td>
<td>64</td>
</tr>
<tr>
<td>EO₃₅PO₇₀EO₂₀</td>
<td>35, 80°</td>
<td>105 (97.5)</td>
<td>780</td>
<td>60</td>
<td>0.80</td>
<td>53</td>
</tr>
<tr>
<td>EO₂₀PO₇₀EO₂₀</td>
<td>35, 80°</td>
<td>103 (99.5)</td>
<td>820</td>
<td>77</td>
<td>1.03</td>
<td>38</td>
</tr>
<tr>
<td>EO₂₀PO₇₀EO₂₀</td>
<td>35, 90°</td>
<td>108 (105)</td>
<td>920</td>
<td>85</td>
<td>1.23</td>
<td>36</td>
</tr>
<tr>
<td>EO₂₀PO₇₀EO₂₀</td>
<td>35, 100°</td>
<td>105 (104)</td>
<td>850</td>
<td>89</td>
<td>1.17</td>
<td>31</td>
</tr>
<tr>
<td>EO₁₃PO₆₅EO₁₇</td>
<td>40</td>
<td>97.5 (80.6)</td>
<td>770</td>
<td>46</td>
<td>0.70</td>
<td>47</td>
</tr>
<tr>
<td>EO₂₆PO₆₀EO₂₀</td>
<td>60</td>
<td>77.6 (77.6)</td>
<td>1000</td>
<td>51</td>
<td>1.26</td>
<td>39</td>
</tr>
<tr>
<td>EO₂₆PO₁₉EO₂₆</td>
<td>40</td>
<td>92.6 (88.2)</td>
<td>960</td>
<td>60</td>
<td>1.08</td>
<td>42</td>
</tr>
<tr>
<td>EO₁₃PO₇₀EO₁₃</td>
<td>60</td>
<td>80.6 (80.5)</td>
<td>950</td>
<td>59</td>
<td>1.19</td>
<td>34</td>
</tr>
<tr>
<td>PO₁₃EO₁₂PO₁₉</td>
<td>60</td>
<td>74.5 (71.1)</td>
<td>1040</td>
<td>48</td>
<td>1.15</td>
<td>34</td>
</tr>
</tbody>
</table>

The two types of mesoporous silica synthesized by Mobil Oil Company in 1992, MCM-41 [188] and MCM-48 [188, 189] have ordered 2-3nm pores. However, large pore-size molecular sieves are much in demand for reactions or separations involving large molecules. Zhao reported the syntheses of well-ordered hexagonal mesoporous silica structures (SBA-15) with tunable large uniform pore sizes up to ~300 Å (Table 1-4, Figure 1-12) which are obtained by use of amphiphilic block copolymers as organic structure-directing agents. In particular, poly(alkylene oxide) triblock copolymers such as poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) are good candidates, because of their mesostructural ordering properties, amphiphilic character, low-cost commercial availability, and biodegradability.
Figure 1-12 TEM images of calcined hexagonal SBA-15 mesoporous silica with different average pore sizes.

Due to the ordered porous structure, tunable pore size and large surface area, mesoporous materials based heterogeneous catalysts were one of the research focuses in the area of heterogeneous catalysts.

1.4 My work/contribution

The recent research, especially in the past 15 years, indicates that Au-based catalysts have great potential because of their unique activity and selectivity for a variety of important reactions. However, the nature of the active Au species/structure/site remains obscure. It has been shown that the reactivity of gold catalysts is very sensitive to sample preparation and pretreatment conditions. This sensitivity makes it difficult to separate the effects of gold particle size from effects of support conditions, which may change as preparation conditions are varied to shift the cluster size distribution. Another problem related with gold catalysts is the poor thermal stability of gold nanoparticles on the surface of support material, which hinders the industrial application of gold catalysts.
However, it is generally accepted that the catalytic activity of Au depends to a large extent on the size of the Au particles, however other effects, such as the nature of the support material, the Au-support interface, the particle shape, and metal-support charge transfer, are purported to be of fundamental importance.

Motivated by the interesting properties of gold catalysts, I designed several comparable catalysts to demonstrate the influence of particle shape, the facet of support and contact interface on the activity in this work. Specifically, I prepared,

1. Gold nanospheres and gold nanorods with similar diameters and variable lengths in an effort to determine the effect of particle sharp.

2. Gold nanoparticles supported on MgO(111) and MgO(100) to illustrate whether the crystal structure of the supports and the electron distribution difference at the interface caused by the structure have an important role in the catalysis process.

3. Gold nanoparticles deposited on Al$_2$O$_3$ aerogel by different methods in an attempt to explain the influence of contact on the thermal stability of particles and thus their activity at high temperature.

4. Gold nanoparticles supported on CeO$_2$@TiO$_2$ which shows high activity in CO oxidation and heptanal oxidation.

5. Gold nanoparticles supported on different metal oxides and their performances in cyclohexane oxidation.
6. Metal gold nanoparticles and cationic gold supported on zeolites which shows totally different activities in cyclization.

7. Silver nanoparticles supported on and the proof of ozone interaction with catalysts.
CHAPTER 2 MATERIALS AND INSTRUMENTS

2.1 Materials

MgO(Active) was ordered from NanoScale Inc. Hydrogen tetrachloroaurate (HAuCl₄·3H₂O, 99.99%), cetyltrimethylammonium bromide (CTAB, 99%), 3-amimopropyl-triethoxysilane (APTES) and all other reagents were obtained from Sigma-Aldrich and used as received. Ultrapure deionized water (Continental Water Systems) was used throughout the experiments.

2.2 Supercritical drying

Supercritical drying is a process to remove liquid in supercritical condition where the fluid has both the gaseous property of being able to penetrate anything, and the liquid property of being able to dissolve materials into their components. Supercritical drying is the most common way to prepare aerogel.

In my experiments, the mixture of toluene/methanol or isopropanol was heated to 265°C and approximately 120-140 bars to become supercritical fluid. Under this condition, the wet gels are still dissolvable in the fluid so that it can maintain the porous structure. The high pressure fluid can be removed all at once like gas without the shrinkage of the porous structure of wet gel.

2.3 Transmission electron microscopy

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is used instead of visible light. Accelerated by high voltage (normally
80-300 KV), electron beam has a much shorter wavelength than visible light. Therefore, high magnification pictures can be obtained from TEM. TEM image is formed from the electrons transmitted through the thin specimen, magnified and focused by an objective lens.

TEM was mainly performed at Fraunhofer IFAM, Germany using a FEI Tecnai F20 S-Twin operated in bright-field TEM (BF-TEM) and high-angle annular scanning TEM (HAADF-STEM) modes at 200 kV with an information limit of 0.15 nm and a nominal spot size of 0.2 nm. The HAADF-STEM mode is based on Z-contrast and therefore widely used to distinguish heavy metals supported on metal oxides. Samples were prepared by spreading an ethanol suspension on carbon coated copper grids and allowing the solvent to evaporate.

Electron tomography is an electron microscopic technique for obtaining a 3-D image from any electron microscopy specimen, whether ordered or not. Electron tomography can be applied to almost any kind of specimen, provided that it is not too thick. There is a thickness, radiation damage and signal to noise dependency. However, it is generally agreed that ~ 4 nm resolution can be obtained from most specimens that are not too thick. There are a number of reviews that can get the reader up to speed on the latest developments.

Data collection for electron tomography involves collecting images while tilting the specimen around a single axis. Usually data can be collected between 70° if the specimen is not too thick. Complete data collection would require tilting through 90° but because at really high tilt angles, the specimen becomes quite thick this is not possible.
There are effectively two ways to collect the images: fixed tilt increments or graduated tilt increments where the tilt increment is proportional to the cosine of the tilt angle. A key feature of electron tomography is the alignment of the tilt series. There are two ways to do this. One of these is called fiducial, or marker, alignment and the other is marker free alignment. The vast amount of tomographic data alignment is done using marker alignment. Excellent software for this is available that is incorporated into a popular segmentation tool. Another method of image alignment is the use of cross-correlation functions. In my tomography, I make exclusive use of cross-correlation functions for image alignment, otherwise known as marker free alignment. An additional problem in electron tomography is the classification of large heterogeneous data sets.

In my experiments, electron tomographic data was obtained in HAADF-STEM mode using a single tilt holder to acquire 151 images over a tilt-range of -75° to 75°. Gold nanospheres (~5nm) were used as markers for alignment. IMOD (software) was used to align the tilt-series using a combination of cross-correlation and marker tracking. The 3D reconstruction was performed in Inspect3D using the SIRT algorithm with 25 iterations. An FEI CM-200 located at Colorado School of Mines was also used to characterize Au/MgO catalysts.

2.4 Surface area and pore structure

Adsorption is a process that a gas or liquid solute accumulates on the surface of a solid or a liquid and forms a film of molecules or atoms. Based on the assumptions that the surface of the adsorbent is uniform, adsorbed molecules do not interact, all adsorption occurs through the same mechanism, only a monolayer is formed even at the maximum
adsorption, Irving Langmuir published a new model isotherm for gases adsorbed on solid surface in 1917 to calculate the surface area of the solid by the amount of gas adsorbed on the solid surface. In 1938 Stephan Brunauer, Paul Emmett and Edward Teller (BET) developed a modified model isotherm taking the multilayer adsorption into condition. The BET method is still a standard method to calculate the surface area of porous materials.

In my work, N₂ adsorption (BET and isothermal measurements) were performed on a Quantachrome Nova 4000e located at Jacobs University Bremen and Micromeritics ASAP 2020 surface area and porosity analyzer located in Colorado School of Mines.

### 2.5 X-ray Diffraction

Powder diffraction (XRD) is a technique used to characterize the crystallographic structure, grain size, and preferred orientation in powdered solid samples. Powder diffraction can be used to identify unknown substances, by comparing diffraction data against a database. By using Scherrer's formula, the grain size can also be estimated according to full-width at half maximum (FWHM). Siemens D5000 diffratometer (Cu Ka, λ=1.5406Å, working at 40kV, 40mA) located at Jacobs University Bremen was used throughout my work.

### 2.6 Diffuse Reflectance Ultraviolet-Visible Spectroscopy

The free electrons in the metal (d electrons in silver and gold) are free to travel through the material. The mean free path in gold and silver is ~50 nm, therefore in particles smaller than this, no scattering is expected from the bulk. Thus, all interactions
are expected to be with the surface. When the wavelength of light is much larger than the
nanoparticle size it can set up standing resonance. Light in resonance with the surface
plasmon oscillation causes the free-electrons in the metal to oscillate. As the wave front
of the light passes, the electron density in the particle is polarized to one surface and
oscillates in resonance with the light's frequency causing a standing oscillation. The
resonance condition is determined from absorption and scattering spectroscopy and is
found to depend on the shape, size, and dielectric constants of both the metal and the
surrounding material. This is referred to as the surface plasmon resonance, since it is
located at the surface. As the shape or size of the nanoparticle changes, the surface
gometry changes causing a shift in the electric field density on the surface. This causes a
change in the oscillation frequency of the electrons, generating different cross-sections
for the optical properties including absorption and scattering. The oscillation frequency of
gold and silver nanoparticles is in UV-vis range. That makes it possible to infer the shape
of gold/silver nanoparticles by the UV-vis spectra. Diffuse reflectance UV-Vis spectra
were recorded on a UV4 (Unicom) spectrophotometer by our cooperators at University of
Bucharest.

2.7 Gas Chromatography

Reaction products were analyzed by gas chromatography (Varian GC-3900) with
a HP-FFAP column (2.5 mm*50 m) and an FID detector, located at Jacobs University
Bremen. The conversion of benzyl alcohol (mol%) was calculated based on moles of
benzyl alcohol converted to benzyl aldehydes, toluene, benzene and the ester. The
selectivity of each product (%) equaled (moles of each product yielded/moles of benzyl
alcohol converted) × 100%. Before GC injection, the acid products were converted into methyl esters.

2.8 Benzyl alcohol oxidation

The liquid phase oxidation of benzyl alcohol over the supported Au catalysts, was carried out in the magnetically stirred 25ml three necks flask, provided with oil bath heating and reflux condenser, at the following general reaction conditions: reaction mixtures=5ml benzyl alcohol+5mg catalysts, reaction time=6 hours, temperature varied from 100 °C to 160 °C in different experiments, 99.9% oxygen was bubbled into the reaction mixture at the speed around 2ml/min.
CHAPTER 3  GOLD NANOPARTICLES SUPPORTED ON MGO(111) NANO-SHEETS AND THEIR ACTIVITY IN THE AEROBIC OXIDATION OF BENZYL ALCOHOL

One of the unique properties of (111) materials is their high surface energy. The highly polarized (111) facets make them an interesting material as support of gold catalysts given the assumption the interface between gold nanoparticles and supporting materials plays an important role in catalytic activity.

I deposited 0.63 wt% gold nanoparticles on the MgO(111) nanosheets and tested their activity in the solvent-free benzyl alcohol aerobic oxidation. N\textsubscript{2} adsorption experiments show that the MgO(111) nanosheets aggregated together during the deposition of gold but they still kept the plate-like structures. For comparison, 0.72wt% gold nanoparticles were deposited on commercially available MgO aerogel-MgO(active) and used to catalyze the reaction. Both TEM and XRD results show that the gold nanoparticles deposited on both types of MgO have the similar size. Those two types of MgO supports also show a similar performance in the oxidation without the deposition of gold. However the gold nanoparticles deposited on MgO(111) shows a significantly higher activity than that deposited on MgO(active) by a factor of \(~5.8\) at \(120^\circ\text{C}\). This high activity can be attributed to oxygen rich surfaces of MgO(111) nanosheets which make the gold nanoparticles electron rich and more active[191] by serving as an electrons supply and transferring electrons to the gold nanoparticles.
3.1 Preparation of gold nanoparticles supported on MgO(111) nanosheet

3.1.1 Synthesis of MgO(111) nanosheets

The MgO(111) was prepared with a modified sol-gel method using 4-methoxybenzyl alcohol to direct the formation of (111) facet [186]. In a typical synthesis of the MgO(111) nanosheet, 1.0 g of thoroughly cleaned Mg scraps was suspended in absolute methanol overnight under the protection of argon atmosphere to form the magnesium methoxide. Then 2.27 g of 4-methoxyl-benzyl alcohol was added to the solution and kept stirring for 5 hours before dropwise adding of the mixture of 1.48 ml H2O and 30 ml methanol to form the sol. After 12 hours stirring, the sol was transferred into a Parr autoclave and supercritically dried after maintenance at 265°C for 12 hours. The obtained aerogel was calcined 6 hours at 500°C to remove the OH group. The final product is an ultrafine white powder.

3.1.2 Preparation of Au/MgO and Au/MgO(111)

To avoid the reconstruction of MgO(111) facet, the deposition of gold was performed in absolute ethanol. Typically, 0.2 g MgO(111) nanosheets were suspended and stirred over night in a 10 ml 1.25 mM HAuCl4/ethanol solution for the deposition of gold. The resulting pink powder was separated by centrifuge and resuspended in 10 ml fresh ethanol. This process was repeated 3 times to remove the unsupported gold particles in solution. The powder was then dried at 120 °C and marked as Au/MgO(111). For the purpose of comparison, gold was also deposited on 0.2 g calcined commercially available MgO aerogels (MgO active) and marked as Au/MgO(active). During the preparation, I
observed that the deposition of gold (color change) on MgO(111) was significantly faster than the deposition on MgO(active).

3.2 Results and Discussion

3.2.1 Characterization of Au/MgO(111) catalysts

The specific surface area ($S_{\text{BET}}$) for Au/MgO(111) showed a significant drop from their parent materials, as showed in Table 3-1. More information can be found in the isothermal patterns (Figure 3-1): the adsorption at low and medium pressure ($P/P_0=0-0.8$) was lost after the deposition of gold, which indicates the loss of micro and mesopores. This is due to the aggregation of MgO(111) nanosheets during the drying process.

Table 3-1 $N_2$-Adsorption data and Au content of different catalysts

<table>
<thead>
<tr>
<th></th>
<th>$S_{\text{BET}}$(m$^2$/g)$^a$</th>
<th>Au Content(wt %)</th>
<th>Au particles size (nm)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO(active)</td>
<td>400</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>MgO(111)</td>
<td>146.06</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Au/MgO (active)</td>
<td>73.81</td>
<td>0.72</td>
<td>3-20</td>
</tr>
<tr>
<td>Au/MgO (111)</td>
<td>32.53</td>
<td>0.63</td>
<td>3-20</td>
</tr>
</tbody>
</table>

$^a$The surface area $S_{\text{BET}}$ is calculated by BET method. $^b$The size of gold nanoparticles is determined by TEM.

However, a H3 type hysteresis loop was found in the isothermal pattern of Au/MgO(111) as well as that of MgO(111). According to the IUPAC classification[192], the H3 hysteresis loop showed that Au/MgO(111) kept the same pore shape with MgO(111), slit-shaped pores which is the non-rigid aggregation of plate-like particles.
Figure 3-1 The isothermal pattern of MgO(111) and Au/MgO(111).

Figure 3-2 shows the wide-angle X-ray diffraction (XRD) patterns of gold catalysts supported on MgO(111) and MgO(active). Those two catalysts have almost the same diffraction patterns especially the peaks of gold, which indicates they have similar gold content and gold particles size.

The two small peaks marked by black dots index to Au and the others index to MgO. The MgO(111) nanosheets were well characterized by HR-TEM in our previous work[186]. Those nanosheets are typically several tens nm in length and width but only 3-5 nm in thickness. By indexing the lattice spacing of side surface, I can conclude that main surface of those nanosheets are (111) facets.
Figure 3-2 The X-Ray diffraction patterns of Au/MgO(111) and Au/MgO(active).

After the deposition of gold, the MgO(111) nanosheets were aggregated together but still showed a sheet-like structure in the overview TEM image shown in Figure 3-3A, (please also compare with Figure 1-10). The deposited gold nanoparticles varied in size. Beside the big particles around 20 nm, lots of tiny particles around 5 nm were also observed. In the HR-TEM image (Figure 3-3B), the sheet-like structure is clearly shown. I am more interested in the nanosheets standing on the copper grids on edge which are marked by red arrows in Figure 3-3B. Judged by their edge, the nanosheets are 3-5 nm in thickness and 20-30 nm in length and width, the same with their parent MgO(111). Combined with the N$_2$ adsorption and TEM results, it can be concluded though the aggregation of MgO(111) nanosheets they kept the same morphologies before and after the deposition of gold.
Figure 3-3  The A) overall and B) high resolution TEM images of the Au/MgO(111). The arrows indicate the MgO(111) nanosheets standing on the grids.

The “standing” nanosheets make it possible to see the interface between gold nanoparticles and MgO(111) nanosheets. However, it is hard to find that the interface considering the low gold content (0.63%) and that the majority of MgO(111) nanosheets are parallel to the grids. Two gold nanoparticles around 10 nm marked as 1 and 2 can be found in Figure 3-3B. Particle 2 is clearly in contact with on a ‘standing’ MgO(111) nanosheet around 5nm thick while particle 1 is located at the edge of an aggregate. Those two particles showed semi-sphere like structure in the view direction and had relative large contact surface with the MgO(111) nanosheets (also see Scheme 1, generated according to the TEM results). Though I did not find how smaller gold particles (3-5nm) contact to the ‘standing’ MgO(111) nanosheets by TEM, I believe they take the same way with 10nm particles as shown in Figure 3-3B.
Figure 3-4 The illustration how 10nm simi-sphere gold nanoparticle contact with the MgO(111) nanosheets.

3.2.2 Aerobic oxidation of benzyl alcohol

The oxidation of benzyl alcohol which is often used as a model reaction for alcohol oxidation, was used in my work to demonstrate the influence of the crystal structure of supporting MgO on the activities. All the reactions were performed in absence of solvent with 6 hours reaction time. No detectable benzene or toluene was produced in the reactions. The catalysis results are showed in Table 3-2.
Table 3-2 Comparative data for solvent-free oxidation of benzyl alcohol. Results were obtained for the oxidation of benzyl alcohol after 6 hours of reaction. The oxidation was carried out by bubbling the oxygen into the reaction mixture (5ml benzyl alcohol and 5mg catalysts) at different temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Catalysts</th>
<th>Conversion (mol.%)</th>
<th>Selectivity (mol. %)</th>
<th>TON*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Benzaldehyde</td>
<td>Benzylic benzoate</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>MgO(Active)</td>
<td>4.07</td>
<td>88.35</td>
<td>11.65</td>
</tr>
<tr>
<td></td>
<td>MgO(111)</td>
<td>4.00</td>
<td>88.89</td>
<td>11.11</td>
</tr>
<tr>
<td></td>
<td>Au/MgO(Active)</td>
<td>1.17</td>
<td>70.45</td>
<td>29.55</td>
</tr>
<tr>
<td></td>
<td>Au/MgO(111)</td>
<td>6.55</td>
<td>92.96</td>
<td>7.04</td>
</tr>
<tr>
<td>120</td>
<td>MgO(Active)</td>
<td>7.84</td>
<td>83.09</td>
<td>16.91</td>
</tr>
<tr>
<td></td>
<td>MgO(111)</td>
<td>7.65</td>
<td>81.53</td>
<td>18.47</td>
</tr>
<tr>
<td></td>
<td>Au/MgO(Active)</td>
<td>3.05</td>
<td>78.21</td>
<td>21.79</td>
</tr>
<tr>
<td></td>
<td>Au/MgO(111)</td>
<td>14.71</td>
<td>82.44</td>
<td>17.56</td>
</tr>
<tr>
<td>140</td>
<td>MgO(Active)</td>
<td>10.24</td>
<td>78.36</td>
<td>21.64</td>
</tr>
<tr>
<td></td>
<td>MgO(111)</td>
<td>11.20</td>
<td>70.15</td>
<td>29.85</td>
</tr>
<tr>
<td></td>
<td>Au/MgO(Active)</td>
<td>3.59</td>
<td>76.84</td>
<td>23.16</td>
</tr>
<tr>
<td></td>
<td>Au/MgO(111)</td>
<td>17.23</td>
<td>56.66</td>
<td>43.34</td>
</tr>
<tr>
<td>160</td>
<td>MgO(Active)</td>
<td>25.55</td>
<td>72.87</td>
<td>27.13</td>
</tr>
<tr>
<td></td>
<td>MgO(111)</td>
<td>24.13</td>
<td>58.01</td>
<td>41.99</td>
</tr>
<tr>
<td></td>
<td>Au/MgO(Active)</td>
<td>7.44</td>
<td>65.74</td>
<td>34.26</td>
</tr>
<tr>
<td></td>
<td>Au/MgO(111)</td>
<td>27.44</td>
<td>47.38</td>
<td>52.62</td>
</tr>
</tbody>
</table>

*Turnover number was calculated as mols of benzaaldehyde /mols of metal after 6 hours.

In the benzyl alcohol oxidation run at 120°C, pure MgO(111) and MgO(active) without gold showed nearly identical performances. Both of them had 7.5-8.0% conversions in 6 hours with 80% selectivity to benzaldehyde. After the deposition of gold, Au/MgO(111) gave a 14.75% conversion nearly twice high as that of MgO(111) while
keeping the same selectivity. On the contrary, Au/MgO(active) showed a performance even worse than its parent MgO(active). The same trend was also showed in the results of reactions operated at 100°C and 140°C. As showed in Table 3-1, during the deposition of gold more than 50% surface area of MgO(111) and MgO(active) was lost especially in the drying process. That may be one of the reasons explain the poor activity of Au/MgO(active). As to Au/MgO(111), I believe its high activities comes from the good contact interface between Au nanoparticles and MgO(111) nanosheets (see details in discussion part).

Operated at higher temperature, better conversion can be obtained from Au/MgO(111) catalyst. But the benzadehyde selectivity also drops dramatically with the temperature because of the over oxidation of benzyl alcohol. At 160°C, it is even less than 50%. Results suggest 120°C is the premium reaction temperature of Au/MgO(111) where it gives a turn over number (TON) of 33577 in 6 hours and keeps a decent selectivity (82.44%) to benzadehyde. That is one of the best performances of reported gold catalysts in the solvent-free oxidation of benzyl alcohol operated at similar conditions.

3.2.3 Density functional theory (DFT) modeling

Density functional theory (DFT) is a quantum mechanical theory used in physics and chemistry to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. With this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron
density. Hence the name density functional theory comes from the use of functionals of the electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry.

Our collaborator, Prof. Cristian Ciobanu from Division of Engineering at Colorado School of Mines helped us to build gold cluster models on MgO(100) and MgO(111) surface by using the super computer at Mines to demonstrate the different state of gold nanoparticles on two types of MgO and therefore to explain the experimental phenomena. Due to the limitation on computer capacity, we did the DFT simulation with 10-atoms gold clusters rather than full-size nanoparticles. However, the DFT simulation does give us some clues.

We have performed structural relaxations at the level of density functional theory (DFT) using the VASP simulation package[193]. The calculations were done in the framework of the generalized gradient approximation (GGA), using projector-augmented wave pseudopotential[194] and the Perdew-Burke-Ernzerhof exchange-correlation energy[195]. We have used MgO surface slabs with the (001), (110), and (111) orientations, with in-plane dimensions of at least 10 Å and a slab thickness of at least 8 Å with the bottom two atomic layers kept fixed. The lattice constant in our calculations was set at the experimental value of $a = 4.2$ Å. In the case of (111)-oriented surfaces, we have relaxed (non-stoichiometric) slabs terminated with the same atomic species on both faces --either with O or with Mg. In all calculations, the vacuum spacing was set to 15 Å, and we used a plane-wave cutoff energy of 450 eV and sampled the Brillouin zone only at the Γ point. The structural relaxations were stopped when the total energy of the slab converged to 0.001 eV. We have relaxed clean slabs as well as slabs with an Au$_{10}$ cluster.
on them, in order to calculate the spatial variation of the electron density due to the presence of the cluster.

Figure 3-5 DFT models of A, gold clusters supported on MgO(100); and B, gold cluster on MgO(111).

Figure 3-5 shows the major geometric difference of gold clusters on two types of MgO surfaces. The iterative arrangement of O and Mg atoms on (100) surface makes the first layer gold atoms (6 atoms) not in the same plane. As shown in Figure 3-5 A, there are 4 atoms are roughly in the same plane with the other 2 atoms are in a higher than those 4. That makes the gold cluster tend to be round at bottom. In case of gold cluster on MgO(111), the first layer 6 gold atoms are almost perfectly in the same plane and the gold cluster shows a perfect pyramid structure with a flat contact surface with the support. That explains why I got semi-sphere gold nanoparticles on MgO(111) (Figure 3-3 B) rather than the sphere gold nanoparticles I got on MgO(100) (Figure 3-3 A).
The electron distribution at the Au/MgO interface can be observed by zooming out the atoms in the DFT models. For each model, the electron distributions at three typical heights (first layer gold atoms, first layer MgO and the right middle of those two layers) were shown in Figure 3-6(Au/MgO(100)) and Figure 3-7(Au/MgO(111)). Comparing those two figures, a major difference comes from the distance between the
first layers of gold and first layers of MgO. This distance is 3.11 Angstroms in case of Au/MgO(111) (A'C' in Figure 3-7), significantly shorter than that in case of Au/MgO(100) (4.88 Angstroms, AC in Figure 3-6) because of the strong attraction from O at the top of MgO(111).

Figure 3-7 Electron distribution on the Au/MgO(111) interface. A, at the height of first layer of gold atoms; C, at the height of top layer of MgO; and B, at the height in middle of those two surfaces.
Therefore, the in-middle electron distribution at Au/MgO(111) interface (Figure 3-7 B) is higher than that at Au/MgO(100) interface (Figure 3-6 B). Even at the height of first layer gold atoms, there is still electron distribution influence around the gold atoms from MgO(111) (Figure 3-7 A) while not significant influence from MgO(100) is observed (Figure 3-6 A). The electron distributions at the height of first MgO layers are also quite different. The electrons are less bounded in Au/MgO(111) model which might facilitate the electron transfer.

To sum up, the DFT simulation indicates the gold clusters are energy preferably sitting on the MgO(111) surface with a flat contact interface and the gold clusters can be 1/3 closer to MgO surface which might facilitate the electron transfer between Au and MgO.

3.2.4 Discussion

The catalysis results indicate the importance of the crystal facet of MgO support for the gold nanoparticles. Since the XRD shows a similar gold particle size exists on both types of MgO support and both types of pure MgO have similar performance in blank reactions, the difference observed in catalytic activity and selectivity may be attributed to the shape of nanoparticles and metal support contact as it has been suggested previously[196, 197]. In a DFT calculation, Rodriguez group[198] found the Au-TiO₂ contact can enhance the chemical activity of the gold nanoparticles by the electrically disturbing them. The electrons from the vacancies of support transfer to the gold nanoparticles through the contact and make them electronically rich[191]. A further calculation shown the O₂ adsorbs preferentially and readily dissociates at the
interface[199]. In case of Au/MgO, Hammer group[200, 201] assume MgO has an active role in the bonding and activation of adsorbates bound to Au and the most active site was formed at the Au-MgO interface whereby several low coordinated Au atoms along with Mg$^{2+}$ cations can interact simultaneously with an adsorbate.

In fact, the semi-spherical gold nanoparticles are sitting on the MgO(111) nanosheets with a relative large contact surface as showed in Figure 3-3B. Considering the highly polarized main surfaces of MgO(111) nanosheets, I assume the gold nanoparticles, thus their activities are influenced in the following ways, i) the O rich main surface facilitates the deposition of Au atom and enhances the Au-MgO interface; ii) the O which dominate the MgO nanosheets main surfaces serves like a large electron supply and makes the gold nanoparticles electron rich and active by transferring electrons though the Au-MgO interface; iii) the large Au-MgO interface as the most active site facilitates the adsorption and activation of oxygen, which is the key step in the gas/liquid oxidation. Those assumptions are supported by our DFT simulation results. Nevertheless, further investigations are needed for a better understanding of the parameters affecting the catalytic activity of aforementioned gold catalysts.
A major problem related with gold catalysts is the poor thermal stability of gold nanoparticles on the surface of support material, which hinders the industrial application of gold catalysts. This problem is even worse in case of using alumina as support material due to the low binding energy between Au and alumina.

In this part of work, I developed a simultaneous synthesis procedure to improve the thermal stability of gold catalysts on alumina, which has much better gold nanoparticle distributions and gets a high activity in benzyl alcohol oxidation.

4.1 Preparation of thermally stable gold nanoparticles supported on Al$_2$O$_3$ aerogel

Ultrastable Au/Al$_2$O$_3$ catalyst with a gold loading of 1.0 wt % was prepared by a simultaneous synthesis method, during which the reduction of Au$^{3+}$ and the hydrolyzation of the aluminium alkoxide took place at the same time. Chloroauric acid was first dissolved in distilled water and then transferred into toluene to form a 0.01M solution (Solution A) with the help of phase transfer agent. In another flask 1.0 gram of aluminium triisopropoxide was dissolved in 50 ml pretreated anhydrous isopropanol and then 50 ml anhydrous toluene was added and kept stirring for 5 hours to form a transparent solution. 10 ml solution A and 0.2 ml APTES was added to this clear solution. After stirring for one more hour, a 15 ml isopropanol solution containing 0.2 ml water and 0.01gram sodium hydroborate was dropwise added to the flask in 30 min. The
gelation process was performed by maintaining stirring for 24 hours at room temperature. The Al₂O₃ gel doped with gold nanoparticles was washed three times by centrifuging and redissolving in isopropanol. Finally the gel was dissolved in 100 ml mixture solution of isopropanol and toluene (1:1 in volume) and dried by supercritical treatment at 265°C (Au/Al₂O₃-Simul). All the samples was calcined at 500°C for 5 hours under the protection of argon.

**Formation of Alumina aerogel (Eq 1)**

\[
\text{Al(OC}_3\text{H}_7)_3 + 3\text{H}_2\text{O} \xrightarrow{\text{Hydrolysis}} \text{Al-sol} \xrightarrow{\text{Gelation}} \text{Al-gel} \xrightarrow{\text{Supercritical Drying}} \text{Al-Aerogel}
\]

**Formation of Gold nanoparticles (Eq 2)**

\[
\text{HAuCl}_4 + \text{NaBH}_4 \xrightarrow{\text{Capping agent}} \text{Gold Nanoparticles}
\]

*Figure 4-1 The two equations in the preparation Au/Al₂O₃- Impreg.*

For comparison, Au/Al₂O₃ was also prepared following the reported method[202]. In a typical experiment, 1.0 gram of Al₂O₃ aerogel was refluxed in 50 ml 9.7 mM Chloroauric acid for 5 hours under 70°C. Then filtered out the powder and resuspended it in 50 ml pure water. After refluxing at 70°C for one hour, the powder was filtered out again, and calcined at 350°C for 5 hours. Finally, light pink powder was obtained, noted as Au/Al₂O₃- Impreg.

**4.2 Results and Discussion**

N₂-ad sorption results show the Au/Al₂O₃ catalyst prepared by simultaneous synthesis (Au/Al₂O₃-Simul) have a large surface area, slightly lower than that of pure Al₂O₃ aerogel (Table 4-1) without doping with gold, which indicates the gold nanoparticles formed in simultaneous deposition process did not influence the formation
of the sol-gel while the impregnation and calcinations process (sample Au/Al₂O₃-Impreg) damaged more than 40% surface area of aerogel. In fact, the destructive influence of solvent to supporting materials is an unavoidable factor in most of the post treatment methods used to prepare heterogeneous catalysts such as deposition and precipitation (DP) and impregnation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcination</th>
<th>( S_{\text{BET}} (\text{m}^2/\text{g}) )</th>
<th>Au Content (wt %)</th>
<th>Size of Au (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/Al₂O₃-Simul</td>
<td>500°C</td>
<td>384</td>
<td>~1.0 (precursor)</td>
<td>3-10 (spheres)</td>
</tr>
<tr>
<td>Al₂O₃ aerogel</td>
<td>500°C</td>
<td>441</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Au/Al₂O₃-Impreg</td>
<td>350°C</td>
<td>252</td>
<td>~1.0 ( {202} )</td>
<td>3-30 (unregular)</td>
</tr>
</tbody>
</table>

\( a \) The surface area \( S_{\text{BET}} \) is calculated by BET method. \( b \) The size of gold nanoparticles is determined by TEM.

### 4.2.1 Structure and morphology of gold nanoparticles in composites

Considering that the Au/Al₂O₃-Simul catalyst was calcined at 500°C, I am extremely interested in the morphology of the gold nanoparticles: i.e. whether they are agglomerated like the typical gold nanoparticles supported on Al₂O₃\( [203, 204] \). In order to increase the contrast between gold nanoparticles and the alumina, scanning transmission electronic microscope (HAADF mode) was utilized to study the morphology and distribution of gold nanoparticles supported on the alumina aerogel. Figure 4-2A shows an overview of the Au/Al₂O₃-Simul catalyst where the uniform gold nanoparticles are evenly distributed on the alumina support. Those gold nanoparticles show a sphere-like structure and are 3-10nm in diameter (Figure 4-2B).
Figure 4-2 HAADF-STEM images of Au/Al₂O₃—Simul the A) overall view, B) higher magnification.

The selected area electron dispersive X-ray (EDX) analysis shown in Figure 4-3, indicates the existence of Si besides Au, Al, O and C (from the carbon film of TEM grids), which is due the APTES used as link agent and the impurity introduced in preparation.
Figure 4-3 selected area Dispersive X-ray (EDX) analysis of Au/Al$_2$O$_3$-Simul.

Figure 4-4 HAADF-STEM images of Au/Al$_2$O$_3$-Impreg.

For comparison, Figure 4-4 shows the Au/Al$_2$O$_3$ catalyst prepared by wet impregnation method. The alumina support shows a similar morphology with that of Au/Al$_2$O$_3$-Simul, which is the typical morphology of alumina aerogel. However, the gold
supported on it shows various shapes and sizes. In addition to the 3-5nm spheres, a large amount of agglomeration is also found with some of them even reaching 30nm.

4.2.2 XANES fitting

The X-ray absorption near edge structure (XANES) fitting revealed that the samples may not have been fully reduced. Extended X-Ray absorption fine structure (EXAFS) fitting to confirm the presence of cationic gold in the Al₂O₃ supported samples. Comparing the “1shell” and “2shell” files for the same sample and same k-weighting should make it apparent that there really is an Au-O shell. The “1shell” files show the fit with the Au-O shell removed and are a worse fit at lower R. One other note: EXAFS fitting is only done over the region where the specific shell is expected to appear, in this case, from about 1.4Å to 3.2Å is where the fit should match the data. The peak that appears at around 0.8Å in every file is a ‘mystery’ peak that always appears in Au EXAFS, but nobody has been able to figure out what it means. The data are shown in Table 4-2.

We also tested CO oxidation on each pellet while it was in the EXAFS cell. For the Al₂O₃ supported catalyst the reaction conditions were 113mL/min total flow with 1% CO and 2.5% O₂. The estimated initial room temperature conversion was 1%, which corresponded to a rate of 0.03 mol CO/(mol Au•min). Because of the design of the EXAFS cell, some unquantifiable bypass during catalytic tests causes the observed rate to be lower than the true rate, thus the numbers above should be used only qualitatively. We estimate this bypass to cause a maximum decrease in observed rate of 50%. However, it is clear that the Au/Al₂O₃ prepared by simultaneous synthesis is active for the oxidation
of CO though we cannot quantify its performance and compare to other catalysts due to the experimental limit.

Table 4-2 Fraction of Au\textsuperscript{3+} and Au\textsuperscript{0} determined by XANES, and parameters of EXAFS characterization: 1st shell coordination number (CN), bond distance (R), Debye-Waller factor (DWF) and inner potential correction (E\textsubscript{0}).

<table>
<thead>
<tr>
<th>Support (Catalyst mass/mg)</th>
<th>Before/After CO Reaction</th>
<th>% Au\textsuperscript{3+}</th>
<th>% Au\textsuperscript{0}</th>
<th>Scatter</th>
<th>CN</th>
<th>R, Å</th>
<th>DWF (x 103)</th>
<th>E\textsubscript{0}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3} (100)</td>
<td>Before</td>
<td>8</td>
<td>92</td>
<td>Au-Au</td>
<td>10.2±0.3</td>
<td>2.87±0.002</td>
<td>1.3±0.005</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Au-O</td>
<td>0.3±0.1</td>
<td>2.05±0.005</td>
<td>0.4±1.5</td>
<td>-</td>
<td>2.0±2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3} (100)</td>
<td>After</td>
<td>8</td>
<td>92</td>
<td>Au-Au</td>
<td>10.2±0.2</td>
<td>2.87±0.002</td>
<td>1.1±0.003</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Au-O</td>
<td>0.4±0.1</td>
<td>2.07±0.005</td>
<td>2.5±1.0</td>
<td>-</td>
<td>1.2±0.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Not surprisingly, both Au/Al\textsubscript{2}O\textsubscript{3}-Simul and Au/Al\textsubscript{2}O\textsubscript{3}-Impreg turned out to be less active than most gold catalysts prepared on reducible metal oxides such as TiO\textsubscript{2}, CeO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3} as they showed in the oxidation of CO. A widely accepted explanation for the poor activity is that Al\textsubscript{2}O\textsubscript{3} has less vacancies which are supposed to be an electron supply for the gold nanoparticles and could make them electron rich and more active. However, the results clearly show two interesting phenomena.

4.2.3 Catalysis performance of ultrastable Au/Al\textsubscript{2}O\textsubscript{3}-Simul

The oxidation of benzyl alcohol which is often used as a model reaction for alcohol oxidation was used in our work to study the activity of the ultrastable Au/Al\textsubscript{2}O\textsubscript{3}
prepared by simultaneous synthesis. All the reactions were performed in absence of solvent with 6 hours reaction time. No detectable benzene or toluene was produced in the reactions. The catalysis results are shown in Table 4-3.

Table 4-3 Comparative data for solvent-free oxidation of benzyl alcohol. Results were obtained for the oxidation of benzyl alcohol after 6 hours of reaction. The oxidation was carried out by bubbling the oxygen into the reaction mixture (5ml benzyl alcohol and 5mg catalysts) at different temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Catalysts</th>
<th>Conversion (mol.%)</th>
<th>Selectivity (mol. %)</th>
<th>Benzaldehyde</th>
<th>Benzyl benzoate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>Au/Al₂O₃ (Simul)</td>
<td>1.76</td>
<td>77.39</td>
<td>22.61</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au/Al₂O₃ (Impreg)</td>
<td>2.03</td>
<td>81.01</td>
<td>18.99</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>Au/Al₂O₃ (Simul)</td>
<td>6.09</td>
<td>88.52</td>
<td>11.48</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au/Al₂O₃ (Impreg)</td>
<td>5.90</td>
<td>84.72</td>
<td>15.28</td>
<td></td>
</tr>
<tr>
<td>140</td>
<td>Au/Al₂O₃ (Simul)</td>
<td>7.40</td>
<td>83.51</td>
<td>16.49</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au/Al₂O₃ (Impreg)</td>
<td>6.77</td>
<td>82.78</td>
<td>17.22</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>Au/Al₂O₃ (Simul)</td>
<td>21.90</td>
<td>72.32</td>
<td>27.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au/Al₂O₃ (Impreg)</td>
<td>10.42</td>
<td>75.96</td>
<td>24.04</td>
<td></td>
</tr>
</tbody>
</table>

Au/Al₂O₃-Simul has a much better performance at high temperature. At 100°C, the Au/Al₂O₃-Simul gives a conversion of even less than that of Au/Al₂O₃-Impreg. Its conversion increases with temperature but no significant advantage over that of Au/Al₂O₃-Impreg was shown at 120 °C and 140 °C. A surge in activity was found at 160 °C, where the conversion of Au/Al₂O₃-Simul is higher than that of Au/Al₂O₃-Impreg.
Both Au/Al₂O₃-Simul and Au/Al₂O₃-Impreg keep a fairly good selectivity to benzaldehyde even at high temperature. In the case of Au/Al₂O₃-Simul, more than 70% selectivity obtained at 160 °C.

4.2.4 Discussion

I attribute the good performance of Au/Al₂O₃-Simul to its stability. In fact, gold is highly mobile on Al₂O₃ surface due to the fact that the Au-Al₂O₃ bond energy is substantially weaker than that of Au-TiO₂ [203] and small gold nanoparticles may be more mobile than atoms[204]. Thus the agglomeration of gold nanoparticles is a serious problem for the Au/Al₂O₃ especially when HAuCl₄ (the most popular and cheapest gold precursor) is involved in the preparation because the Cl⁻ can significantly accelerate the agglomeration process[205]. Figure 4-4 clearly shows the aggregation of gold deposited on Al₂O₃ by a typical wetness impregnation method calcined at 350 °C in air. Though the oxidation of benzyl alcohol is run at relatively low temperature, the agglomeration may be even higher due to the influence of the hot solvent. We noted that the 1D or 2D agglomeration of gold on Al₂O₃ is even notable at room temperature[203]. As shown in Figure 4-5, in the simultaneous synthesis process, the reduction of gold takes place at the same time with the hydrolyzation and condensation of metal alkoxide and APTES. Two additional factors to stabilize the gold nanoparticles can be expected from this process, i) the amino head of APTES can help the distribution of Au³⁺ by anchoring it; ii) when gold nanoparticles formed, with the Si head condensed with the Al₂O₃ support and the well-known affinity between its amino head and gold surface, the APTES can increase the interface between gold and Al₂O₃ to stabilize gold nanoparticles; iii) though the APTES functional group was damaged after calcination at 500 °C, the enhanced interfaces are
still there to hamper the mobility of gold nanoparticles. Therefore, the well stabilized gold nanoparticles show better performance than Au/Al₂O₃-Impreg at 160 °C.

Figure 4-5 The scheme of simultaneous synthesis process for Au/Al₂O₃-Simul. The arrow marked as ‘1’ stands for the start of reduction gold Au, hydrolyzation and condensation of metal alkoxide and APTES; the arrow marked as ‘2’ stands for the 5 hours calcination process at 500°C.
CHAPTER 5 GOLD NANOPARTICLES SUPPORTED ON CEO2-TIO2 COMPOSITE AS HIGHLY ACTIVE CATALYSTS FOR CO OXIDATION AND THE SELECTIVE OXIDATION OF HEPTANAL

Oxide materials containing ceria (CeO₂) have been the subject of numerous investigations in recent years because of their wide range of applications in catalysis and materials science[206, 207]. The redox and catalytic properties of CeO₂ are profoundly enhanced when used in combination with other transition metal or rare earth oxides[208]. Among various elements, the introduction of zirconium into the ceria lattice has been particularly effective in the enhancement of the overall performance of CeO₂. In fact, ceria–zirconia mixed oxides have been regarded as potential substitutes for ceria in the formulation of new generation three-way catalysts (TWC) on the basis of their superior catalytic properties resulting from the combination of oxygen storage characteristics of ceria and superior refractory properties of zirconia. The ceria–zirconia mixed oxides exhibit several advantages over pure ceria, which include high thermal resistance, improved reduction efficiency of the Ce⁴⁺/Ce³⁺ redox couple[209], and excellent oxygen storage/release capacity (OSC).

Other significant applications of ceria-based materials apart from TWC include fuel cell processes, oxygen permeation membrane systems, degradation of nitric oxides (deNOₓ) catalysis, exhaust combustion catalysts, and catalytic wet oxidation[210]. Mainly ceria-based noble metals are employed for various catalytic applications because of their increased reactivity. Nevertheless, ceria-based transition metal oxides are the best option because these are much cheaper than noble metals, allowing a higher catalyst load which
can compensate for the reduced reactivity. However, such approaches are very limited in the literature.

Motivated by the unique and favorable characteristics of ceria-based mixed oxides for various catalytic applications as discussed above[211], the present systematic investigation was undertaken. In this work, the catalytic activity evolution of Au nanoparticles over the surface of CeO$_2$–TiO$_2$ support was investigated.

5.1 Preparation of Catalysts

5.1.1 Preparation of Au/TiO$_2$@CeO$_2$

TiO$_2$@CeO$_2$ substrate (90 wt% TiO$_2$–10 wt% CeO$_2$, respectively) were prepared by the sol–gel method using titanium $n$-butoxide (Aldrich 97 wt%) and cerium nitrate (Aldrich 99.9 wt%) as essential reactants. Ethanol (99 wt%) was chosen as the solvent medium of the latter substances and a molar alkoxide/solvent ratio of 1/16 was selected. The mixture was kept refluxing while adjusting to pH=3 with HNO$_3$ during the entire sol synthesis. Afterwards, water, in a molar proportion of 1:8 with respect to the Ti alkoxide, was added dropwise during a period of 4 h. The reactant mixture was kept refluxing until a gel was formed. Then the gel was dried by supercritical treatment at 265°C and calcined at 500°C for 8 hours. Finally gold was deposited on prepared TiO$_2$@CeO$_2$ substrate at PH=10.0 using DP method.
5.1.2 Preparation of Au/TiO₂

For comparison, TiO₂ aerogel without doping CeO₂ was prepared by the same procedure without adding cerium nitrite. Gold nanoparticles were also deposited on prepared TiO₂ substrate at PH=10.0 using DP method.

5.2 Results and Discussion

5.2.1 Characterization of Au/TiO₂@CeO₂ and Au/TiO₂ catalysts

The specific surface area (S_{BET}) for TiO₂@CeO₂ and Au/TiO₂ catalysts showed a slight drop from their parent materials, as showed in Table 5-1. This is due to the aggregation of MgO(111) nanosheets during the drying process. But the Au/TiO₂@CeO₂ still has a high surface area of 92 (m²/g) while the surface area of Au/TiO₂ goes 154(m²/g).

<table>
<thead>
<tr>
<th></th>
<th>S_{BET}(m²/g)</th>
<th>Au Content(wt %)</th>
<th>Au particles size</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂@CeO₂</td>
<td>98</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Au/TiO₂@CeO₂</td>
<td>92</td>
<td>~2 wt % (precursor)</td>
<td>3-5 nm (by TEM)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>227</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>Au/TiO₂</td>
<td>154</td>
<td>~2 wt % (precursor)</td>
<td>3-5 nm [78]</td>
</tr>
</tbody>
</table>

The surface area S_{BET} is calculated by BET method.

The gold nanoparticles in catalysts are typically less than 5 nm (Figure 5-1). In a high magnification TEM image, the lattice of gold nanoparticles can be observed. The overlapped different lattice can also be observed from support materials which indicate that the TiO₂ and CeO₂ form a uniform system.
Figure 5-1 TEM picture of Au/TiO$_2$@CeO$_2$ (The inset is a image with low magnification).

Figure 5-2 shows the wide-angle X-ray diffraction (XRD) patterns of gold catalysts supported on TiO$_2$@CeO$_2$ and the pure Au/TiO$_2$@CeO$_2$ without gold. Those two samples have almost the identical diffraction patterns and no peaks of gold were observed in the pattern because the Au(111) peak, the strongest peak for gold is buried in the peak of TiO$_2$ (004). This proofs that the gold nanoparticles are small enough to not show strong peak at $38^\circ$ compare with TiO$_2$ particles. The particle sizes of TiO$_2$ and CeO$_2$ are estimated to be 11.4 nm and 16.1 nm individually calculated by Scherrer’s equation.
Figure 5-2 The X-Ray diffraction patterns of TiO$_2$@CeO$_2$ and Au/TiO$_2$@CeO$_2$.

The XANES fitting revealed that the samples may not have been fully reduced. There are small amount of cationic gold in this catalyst. Even after reduction by passing through CO, there is still around 2% cationic gold.

Table 5-2 Fraction of Au$^{3+}$ and Au$^0$ determined by XANES.

<table>
<thead>
<tr>
<th>Support (Catalyst mass/mg)</th>
<th>Before/After CO Reaction</th>
<th>XANES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TiO$_2$@CeO$_2$ (100)</td>
<td>Before</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>96</td>
</tr>
<tr>
<td>Au/TiO$_2$@CeO$_2$ (100)</td>
<td>After</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>98</td>
</tr>
</tbody>
</table>
5.2.2 Catalytic activity of Au@TiO$_2$/CeO$_2$

The CO oxidation over Au/TiO$_2$@CeO$_2$ catalysts was performed at Mannheim University by one of our collaborators. The mixture of 1 vol% CO and 99 vol% air was pushed through 50mg Au/TiO$_2$@CeO$_2$ at different temperature with a speed of GHSV (gas hourly space velocity) = 80000 mL g$^{-1}$ h$^{-1}$. The tests have been performed both in gradient and isothermal conditions. The results show that the gold nanoparticles supported on TiO$_2$@CeO$_2$ is highly active for the CO oxidation. At -10°C, the CO achieves 50% conversion (Figure 5-3). This result is comparable with the best gold catalysts for the CO oxidation (Figure 1-1).

![Figure 5-3 The CO oxidation catalyzed by Au/TiO$_2$@CeO$_2$. Reaction condition: Catalyst: 50mg; Feed composition: 1 vol% CO in air; Speed: GHSV = 80000 mL g$^{-1}$ h$^{-1}$.](image-url)
Figure 5-4 Conversion of n-heptanal in the catalytic oxygen reaction over different catalysts at A) 25 ºC and B) 50 ºC.
In the benzyl alcohol oxidation, both Au@TiO$_2$/CeO$_2$ and Au@TiO$_2$ give a conversion around 10% and selectivity around 80%. No significant difference is found between those two catalysts in this reaction.

The selective oxidation of n-heptanal was used to compare the activity of Au/TiO$_2$@CeO$_2$ and Au/TiO$_2$. The oxidation was performed at two temperature 25°C and 50°C (Figure 5-4). The results shown Au/TiO$_2$ is almost inert for this reaction. The conversions with/without Au/TiO$_2$ are almost same, while the Au/TiO$_2$@CeO$_2$ catalyst has the highest conversion at 25 °C. The TiO$_2$@CeO$_2$ without gold also shows some activity compare to the blank reaction. That indicates the CeO$_2$ is an active component for the oxidation of hepatal. The gold nanoparticles supported on TiO$_2$@CeO$_2$ can accelerate the reaction while the gold nanoparticles supported on TiO$_2$ shows no activity. That might be related to the high-efficiency Ce$^{4+}$/Ce$^{3+}$ redox couple and the electron transfer between gold nanoparticles and CeO$_2$.

5.2.3 Discussion

Motivated by the unique and favorable characteristics of ceria-based mixed oxides for various catalytic applications, I prepared gold catalysts supported on TiO$_2$@CeO$_2$ composite. This catalyst is highly active in the CO oxidation. In the oxidation of heptanal, gold supported on TiO$_2$@CeO$_2$ shows better activity than those supported on TiO$_2$. I believe this is caused by the Ce$^{4+}$/Ce$^{3+}$ redox couple and the electron transfer between gold nanoparticles and CeO$_2$ which facilities the activation of oxygen therefore accelerate the oxidation process. However, I did not observe the same phenomena in benzyl alcohol. Gold nanoparticles supported both on TiO$_2$@CeO$_2$ and TiO$_2$ show very similar activity. More research works are required to get more insight about the role of CeO$_2$. 

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CHAPTER 6 CATALYTIC OXIDATION OF CYCLOHEXANE BY OXYGEN OVER GOLD NANOPARTICLES SUPPORTED ON DIFFERENT SUBSTRATES

The selective oxidation of alkanes utilizing molecular oxygen is a challenging problem. The production of more valuable oxidized products in relation to the low-cost raw materials is economically interesting. Molecular oxygen is the cheapest and has the highest content of active oxygen. It is necessary to find a good catalyst to activate the reaction between oxygen and cyclohexane. However, the technology with which cyclohexane is oxidized by $O_2$ to produce cyclohexanone and cyclohexanol has not been improved over the years.

Recently, Richards' group found that nanoparticles immobilized on SBA-15 by different methods had a good performance to catalyze the aerobic oxidation of cyclohexane in solvent free system[149]. Considering the properties of substrates are one of the key infector to the activity of heterogeneous catalysts, three gold catalysts with different substrates were prepared and studied in order to further increase the conversion and selectivity.

In this chapter, Au/Al$_2$O$_3$ refers to a gold catalyst supported on alumina (an acidic oxide), which was prepared by a simultaneous synthesis method and had a good gold distribution. Au/TiO$_2$@CeO$_2$ is a gold catalyst immobilized on neutral oxides-titanium oxides doped with ceria by a well known deposition and precipitation (DP) method. Titanium oxides are also the best reported substrate for gold catalysts in CO oxidation. Based on magnesium oxides with novel facet structure, reported by Richards' group recently, Au/MgO(111) was also prepared and used as a gold catalyst supported on basic
substrates. The preparation and characterization of those catalysts were described in previous chapters.

6.1 Oxidation of cyclohexane

The catalytic oxidation of cyclohexane with molecular oxygen was carried out in stainless Parr high-pressure reactors with mechanical stirrers. Typically, measured amount of cyclohexane and catalyst were added into the reactor, which was first purged with oxygen for 5 min, then charged with oxygen to desired pressure, sealed and heated to the desired temperature. When the reaction was completed, the reactor was cooled down to room temperature in air and then the pressure was released slowly. Thereafter, a certain quantity of methanol was added into the reactor to dissolve the products and the solid catalyst was filtered off. The products were analyzed by gas chromatography (Varian GC-3900) with a HP-FFAP (25mm*50m) column and an FID detector. The acids in products were converted into ester before GC analysis using a reported method [11]. In those reactions performed below 130°C, chlorobenzene was used as internal standard to quantify the components.

The conversion of cyclohexane (mol%) was calculated based on moles of cyclohexane converted to cyclohexanone, cyclohexanol, and diacids. The selectivity of each product (%) equaled (moles of each product yielded/moles of cyclohexane converted) × 100%.
6.2 Results and discussion

6.2.1 Catalytic activity of gold nanoparticles supported on different substrates

The oxidation of cyclohexane was carried out at 150 °C for 6 h without any initiator under the pressure of 15 bar O₂ over gold catalysts and their pure substrates without gold. The reaction results are listed in Table 6-1.

Table 6-1 The oxidation of cyclohexane catalyzed by gold catalysts supported on different substrates. Reaction condition: temperature 150 °C; pressure, 15 bar O₂; time, 6 h; the amount of catalyst, 50 mg; the amount of cyclohexane, 25ml; reactor capacity, 330 ml.

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃</th>
<th>Au/Al₂O₃</th>
<th>TiO₂@CeO₂</th>
<th>Au/ TiO₂@CeO₂</th>
<th>Au/MgO(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion (mol%)</td>
<td>5.84</td>
<td>20.16</td>
<td>10.99</td>
<td>14.81</td>
<td>20.04</td>
</tr>
<tr>
<td>Selectivity (K+A)</td>
<td>91.63</td>
<td>34.92</td>
<td>63.55</td>
<td>52.28</td>
<td>51.90</td>
</tr>
<tr>
<td>Cyclohexanol (A) (mol%)</td>
<td>39.28</td>
<td>15.36</td>
<td>27.05</td>
<td>24.82</td>
<td>21.68</td>
</tr>
<tr>
<td>Cyclohexanone(K) (mol%)</td>
<td>52.35</td>
<td>19.56</td>
<td>36.50</td>
<td>27.46</td>
<td>30.23</td>
</tr>
<tr>
<td>Formic acid (mol%)</td>
<td>0.00</td>
<td>6.74</td>
<td>4.11</td>
<td>0.00</td>
<td>5.45</td>
</tr>
<tr>
<td>Acetic acid (mol%)</td>
<td>0.00</td>
<td>3.50</td>
<td>1.75</td>
<td>1.87</td>
<td>2.32</td>
</tr>
<tr>
<td>Butyric acid (mol%)</td>
<td>0.00</td>
<td>0.24</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Valeric acid (mol%)</td>
<td>4.03</td>
<td>1.26</td>
<td>2.05</td>
<td>0.24</td>
<td>1.25</td>
</tr>
<tr>
<td>Caproic acid (mol%)</td>
<td>2.08</td>
<td>0.70</td>
<td>1.37</td>
<td>0.14</td>
<td>0.84</td>
</tr>
<tr>
<td>Succinic acid (mol%)</td>
<td>0.00</td>
<td>1.69</td>
<td>1.84</td>
<td>1.60</td>
<td>2.44</td>
</tr>
<tr>
<td>Glutaric acid (mol%)</td>
<td>0.00</td>
<td>5.25</td>
<td>4.27</td>
<td>4.79</td>
<td>6.35</td>
</tr>
<tr>
<td>Adipic acid (mol%)</td>
<td>2.09</td>
<td>19.78</td>
<td>11.89</td>
<td>20.33</td>
<td>15.47</td>
</tr>
<tr>
<td>Unknown (mol%)</td>
<td>0.16</td>
<td>25.92</td>
<td>9.17</td>
<td>18.75</td>
<td>13.98</td>
</tr>
</tbody>
</table>
When pure substrates were added, the conversion is low. However, once gold catalysts were applied, the oxidation reaction between cyclohexane and pure molecular oxygen was immediately initiated. As shown in Table 6-1, the catalytic activity of all the gold catalysts gradually decreased in the sequence of Au/Al₂O₃ > Au/MgO(111) > Au/TiO₂@CeO₂. Within 6 h, about 10–20 mol% of cyclohexane was effectively converted to the products of cyclohexanol and cyclohexanone (KA-oil). The total selectivity of KA-oil varied in the range of 34.92–52.28%, accompanied with a decreasing order of Au/TiO₂@CeO₂ > Au/MgO(111) > Au/Al₂O₃. Considering the 15-20% adipic acids in products which is also a useful intermediate, the percentage of useful products (KA-oil and adipic acid) are about 53.8%-71.03%. No appreciable amount of the intermediate CHHP was detected in all the reactions, possibly related to their high activity.

Under 150 °C, 15 bar oxygen; the gold catalysts showed a good activity in cyclohexane oxidation, but over-oxidation also happened under this condition which resulted in the increase of diacids and the drop of selectivity. Therefore reactions were also performed under lower temperature and oxygen pressure using TiO₂@CeO₂ as catalyst to search a proper reaction condition. In those experiments, small amount of TBHP (0.7% of cyclohexane) was added as initiator. Table 6-2 showed the conversion increased with temperature and the reaction time, which reached 3.83 at 130°C after 8 hours reaction. In those experiments, no detectable diacids were found in the GC analysis.

The oxidation over gold catalysts was also carried out at atmosphere pressure. Table 6-3 showed the conversion in all the experiments was below 0.7%-the amount of
TBHP, which probably meant the molecular oxygen did not take part in the oxidation of cyclohexane under this condition.

Table 6-2 The oxidation of cyclohexane over TiO2@CeO2 at low pressure and temperatures. Reaction conditions: cyclohexane, 7 ml; the amount of catalyst, 20 mg; TBHP(70%), 0.1 ml; K, cyclohexanone; A, cyclohexanol; CHHP, cyclohexyl hydroperoxide; reactor capacity, 25 ml.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pressure</th>
<th>Time</th>
<th>Yield (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>100°C</td>
<td>7.5 Bar</td>
<td>4 h</td>
<td>0</td>
</tr>
<tr>
<td>100°C</td>
<td>7.5 Bar</td>
<td>8 h</td>
<td>0</td>
</tr>
<tr>
<td>110°C</td>
<td>7.5 Bar</td>
<td>4 h</td>
<td>0</td>
</tr>
<tr>
<td>110°C</td>
<td>7.5 Bar</td>
<td>8 h</td>
<td>0</td>
</tr>
<tr>
<td>120°C</td>
<td>7.5 Bar</td>
<td>4 h</td>
<td>1.04</td>
</tr>
<tr>
<td>130°C</td>
<td>7.5 Bar</td>
<td>4 h</td>
<td>1.04</td>
</tr>
<tr>
<td>130°C</td>
<td>7.5 Bar</td>
<td>8 h</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 6-3 The oxidation of cyclohexane at atmosphere pressure. Reaction conditions: a 25 ml flask equipped with oil bath, magnetic stirrer and condenser was used as oxidation reactor; a balloon filled with oxygen was connected at the top of condenser to supply the required oxygen in reaction; reaction time, 8 h; cyclohexane, 7 ml; the amount of catalyst, 20 mg; TBHP (70%), 0.1 ml; K, cyclohexanone; A, cyclohexanol; CHHP, cyclohexyl hydroperoxide.

<table>
<thead>
<tr>
<th>Temp</th>
<th>Au/Al2O3</th>
<th>Au/TiO2@CeO2</th>
<th>TiO2@CeO2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CHHP</td>
<td>A K Total</td>
<td>CHHP A K Total</td>
</tr>
<tr>
<td>100 °C</td>
<td>0.59</td>
<td>0 0 0.59</td>
<td>0 0.5 0.11 0.61</td>
</tr>
<tr>
<td>130 °C</td>
<td>0.56</td>
<td>0 0 0.56</td>
<td>0 0.64 0.09 0.73</td>
</tr>
</tbody>
</table>
6.2.2 Summary

Three gold catalysts individually supported on acidic, neutral and basic substrates were prepared and studied in the aerobic oxidation of cyclohexane. Results showed that they have a good activity at high temperature (120-150°C) and high pressure (7.5-15 bar oxygen) while no evidence showed that the molecular oxygen took part in the oxidation of cyclohexane at atmosphere pressure.
CHAPTER 7 NEW HETEROGENEOUS GOLD CATALYSTS IN THE EFFICIENT ACCESS TO FUNCTIONALIZED LACTONES[212]

This work is done as cooperation between Richards’ group and Prof. Vasile I. Parvulescu’s research group in Romania. I prepared the catalysts and did the TEM analysis and some other characterization. The catalytic part work was mainly done by Florentina Neatu from Prof. Vasile I. Parvulescu’s research group.

As I mentioned in previous chapters, the work of Haruta [83] and Hutchings [213] pioneered the interest for gold in heterogeneous catalysis, showing that it can catalyze the CO oxidation at low temperatures and ethyne hydrochlorination. The interest for this element thus expanded, numerous contributions demonstrating its effectiveness as supported metal in many other important reactions. Very recently, Corma and Serna[214] reviewed the behavior of gold nanoparticles in catalysis showing that they may act as active redox catalyst for oxygen-containing hydrocarbons, as reduction catalyst for alkenes, alkynes, imines, carbonyls, and nitro compounds. Au/TiO₂ and Au/Fe₂O₃ proved to be effective in hydrogenation of nitro compounds, also providing an alternative catalytic route for the production of cyclohexanone oxime. It was also shown that it is possible to modify the reactivity of the small particles of gold by supporting these on a CeO₂ nanocrystalline support leading to very active catalysts for CO oxidation and homocoupling of aryl boronic acids. The performances of these catalysts were assigned to stabilized Au³⁺, which were considered as active sites for performing not only the oxidation of CO but also the C–C bond formation. On the other side nanocrystalline Au particles deposed on a more neutral support like carbon can provide tunable active catalysts for the oxidation of alkenes using air, with high selectivity to partial oxidation.
products and significant conversions without any sacrificial reductant.\cite{6} Anticipating that heterogeneous gold catalysts may be active for C-O bond formations, we wish to report therein the preparation and unprecedented study of the activity of some gold supports for the cyclization of carboxylic acids to lactones.

### 7.1 Preparation of catalysts

We chose to immobilize gold on various supports by precipitation of AuCl\textsubscript{3} with NaOH on nanocrystalline CeO\textsubscript{2}, MgO, or TiO\textsubscript{2}. Taking in account the literature data concerning the role of Au\textsuperscript{III} in oxidation reactions we also decided to prepare a gold exchanged beta zeolite. Simple depositions/precipitations on a zeolite BEA in the H or NH\textsubscript{4}\textsuperscript{+} forms were realized and led to the corresponding Au/beta and Au/betaNH\textsubscript{4}\textsuperscript{+}. The resulted catalysts were characterized by ICP-AES, adsorption-desorption isotherms of N\textsubscript{2} (Table 7-1).

**Table 7-1 The characterization of catalysts.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Au loading, wt%</th>
<th>Surface area, m\textsuperscript{2}g\textsuperscript{-1}</th>
<th>Average Au particle, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta zeolite</td>
<td>4</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td>Au/betaNH\textsuperscript{4+}</td>
<td>4</td>
<td>318</td>
<td>3—5</td>
</tr>
<tr>
<td>Au/beta</td>
<td>4</td>
<td>294</td>
<td></td>
</tr>
<tr>
<td>Au/CeO\textsubscript{2}</td>
<td>4</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>Au/MgO</td>
<td>2</td>
<td>62</td>
<td>5—7</td>
</tr>
<tr>
<td>Au/TiO\textsubscript{2}</td>
<td>4</td>
<td>42</td>
<td></td>
</tr>
</tbody>
</table>

Au/TiO\textsubscript{2}, Au/MgO, and Au/CeO\textsubscript{2} were prepared in a similar way. Standard procedure for the catalytic tests was: a mixture of 0.26 mmol acetylenic acid, 20 mg gold catalyst in acetonitrile (1.2 mol L\textsuperscript{-1}) was stirred under air atmosphere at room temperature or 40\textdegree C. After completion of the reaction, the mixture was centrifugated. By simple
décantation the catalyst was removed from the reaction mixture and the solvents were evaporated under reduced pressure to give the corresponding lactone. $^1$H NMR and $^{13}$C NMR were recorded on a Bruker AV 300 instrument and were in accordance to the literature.

We then studied the efficiency of such gold supports for C-O bond formation. We selected the Au-catalyzed cycloisomerization of carboxylic acetylenic acids as a standard reaction. The catalysts were prepared following the next procedure: 1g of beta zeolite was vigorously stirred for 3h with 100 ml solution of NH$_4$NO$_3$ 1M at 353 K. The slurry was filtrated and carefully washed, then dried for 6 h at 333 K and calcined for 24 h at 773 K. Au-supported catalysts were prepared by deposition-precipitation method, by adding the support (1g) to an aqueous solution of HAuCl$_4$ ($10^{-3}$ mol L$^{-1}$) previously adjusted at pH=8.5 with a NaOH solution (0.2 mol L$^{-1}$). The slurry was maintained at 343 K, under vigorous stirring for 3 h. After stirring, the sample was filtered, washed with deionized water until elimination of chloride, and then dried under vacuum at 333 K for 24 h.

7.2 Results and discussion

We indeed recently described the catalytic properties of AuCl for the synthesis of functionalized lactones. Nevertheless, the optimized system still needed 2-5 mol% of gold and was limited to gem-substituted substrates. Some other reports described similar cyclizations but the presence of a base was necessary to achieve the reaction.

7.2.1 Cyclization of the standard acetylenic substrate

Based on this background, we decided to check the behavior on 4 wt% Au catalysts in the cyclization of the standard acetylenic substrate 1a (Table 7-2).
Table 7-2 Au-catalyzed cyclization of carboxylic acid.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion [%]</th>
<th>Yield [%]</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Au/CeO₂</td>
<td>0</td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Au/MgO</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3[a]</td>
<td>Au/MgO</td>
<td>80</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Au/TiO₂</td>
<td>50</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Au/beta</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Au/betaNH₄⁺</td>
<td>100</td>
<td>99</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>betaNH₄⁺ or Hβa</td>
<td>0</td>
<td>/</td>
<td></td>
</tr>
</tbody>
</table>

Note: [a] 40 °C, 16 h [b] isolated yield.

The cyclization of acetylenic acids does not take place over gold supported on CeO₂ or MgO (Table 7-2, entries 1-2) at room temperature after 8h. The main effect of increasing the temperature and time for the reaction proceeded over Au/MgO catalyst with the decomposition of the substrate and the formation of only 34% of the desired product (Table 7-2, entry 3). Such a behavior was rather surprising since CeO₂ and even more, MgO exhibit basic properties as supports, that in agreement with the literature should help this reaction. The Au/TiO₂ catalyst presented a moderate activity at room temperature after 8h (Table 7-2, entry 4). Considering that a gold exchanged beta zeolite may behave as an halide substitute due to its acidity properties we then test the efficiency of Au/beta and Au/betaNH₄⁺ (Table 7-2, entries 5-6). No conversion was observed in the presence of Au/beta (Table 7-2, entry 5). We were pleased to find that Au/betaNH₄⁺ exhibited a high activity, as 99% of the γ-lactone 2a was isolated. It is worth to notice
that the experiments performed using pure zeolite (ie without any Au) either in the H or NH$_4^+$ form, or on BEA treated in a solution with a pH corresponding to those at which the deposition/precipitation process was carried out led to zero conversion in this reaction (Table 7-2, entry 7). Moreover, the reaction was found to be very slow when conducted under argon and the best yields were obtained under air conditions.

7.2.2 Cyclization of the functional acetylenic substrate

The scope of the reaction was then studied for various acetylenic acids either at room temperature or at 40 °C (Table 7-3). We first evaluate the efficiency of the system on malonic derivatives 1b-1e (Table 7-3, entries 1-6). Very good yields were observed for the cyclizations of acetylenic carboxylic acids 1b-1d bearing alkyl or alkenyl side chains (Table 7-3, entries 1-4). As expected, we observed that the reaction times were longer than under homogeneous conditions. Nevertheless, it’s noteworthy that the catalyst loading is very low and is estimated to 1.5 mol% of gold per reaction. No side reactions were observed on the alkenyl side chains during the course of the reaction at 40°C (Table 7-3, entries 2-4).

The presence of a benzyl group also allowed a clean cyclization leading to the lactone in 71% isolated yield (Table 7-3, entry 6). Encouraged by such results, we tried to transform the unsubstituted substrates, for which only degradation or formation of methylketone had been observed under homogeneous conditions. The cyclization of 2-prop-2-ynyl-malonic acid monomethyl ester 1f (Table 7-3, entries 7-8) needed a prolonged reaction time and a temperature of 40°C to get to complete conversion. The corresponding lactone 2f was isolated in a modest yield of 50%, which may be due to the
degradation of starting material. Indeed, in the case of the 2-phenyl-pent-4-ynoic acid 1h the corresponding *exo*-methylene lactone was obtained in 80% yield (Table 7-3, entry 9).

**Table 7-3 Gold-catalyzed cycloisomerization of functionalized carboxylic acids.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>T [°C]</th>
<th>Yield [%]</th>
<th>Conv. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;Et</td>
<td>n-Bu</td>
<td>2b</td>
<td>RT</td>
<td>60 (90)</td>
</tr>
<tr>
<td>2&lt;sup&gt;[a]&lt;/sup&gt;</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;Et</td>
<td>n-Bu</td>
<td>2b</td>
<td>40</td>
<td>85 (100)</td>
</tr>
<tr>
<td>3</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>but-2-enyl</td>
<td>2c</td>
<td>40</td>
<td>80 (100)</td>
</tr>
<tr>
<td>4</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>allyl</td>
<td>2d</td>
<td>40</td>
<td>88 (100)</td>
</tr>
<tr>
<td>5</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;Et</td>
<td>Bn</td>
<td>2e</td>
<td>RT</td>
<td>65 (70)</td>
</tr>
<tr>
<td>6</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;Et</td>
<td>Bn</td>
<td>2e</td>
<td>40</td>
<td>71 (100)</td>
</tr>
<tr>
<td>7&lt;sup&gt;[a]&lt;/sup&gt;</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>H</td>
<td>2f</td>
<td>RT</td>
<td>25 (40)</td>
</tr>
<tr>
<td>8&lt;sup&gt;[a]&lt;/sup&gt;</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>H</td>
<td>2f</td>
<td>40</td>
<td>50 (100)</td>
</tr>
<tr>
<td>9</td>
<td>H</td>
<td>Ph</td>
<td>2g</td>
<td>40</td>
<td>80 (85)</td>
</tr>
<tr>
<td>10</td>
<td>CO&lt;sub&gt;2&lt;/sub&gt;Me</td>
<td>cinnamyl</td>
<td>2h</td>
<td>40</td>
<td>99 (100)</td>
</tr>
</tbody>
</table>

**Note: [a] 16 h [b] isolated yield**

The reaction of a bis-homopropargylic acid 1h was also particularly challenging to prepare 8-butyrolactones. The cyclization of 8-acetylenic acid was extremely clean and lead exclusively to the *exo*-lactone 2h in 99% isolated yield (Table 7-3, entry 10). Even though the catalyst loading was low, the recycling of the gold support was tested in the case of the cyclization of 1a. After centrifugation, the catalyst was recovered and could
be used 5 times without any loss in activity. The analysis of the mother liquor indicated no leaching of gold into the solution.

**7.2.3 XPS and TEM analysis of catalysts**

A rationalization of the observed results was then tempted through more specific analysis of the effective catalyst. Figure 7-1 shows the TEM images and Energy dispersive X-ray analysis (EDX) of Au/betaNH₄⁺ support. A quite narrow size distribution with the maximum centered at 3-5 nm can be observed from the bright-field TEM picture. As shown from Figure 7-1 the morphology of the zeolite support was preserved. Based on an atomic-number (Z) sensitive nature of the high-angle annular dark-field (HAADF) contrast (Z-contrast), ADF-STEM picture offered a better gold/zeolite contrast and revealed the existence of some gold nanoparticles below 3 nm. EDX analysis of the crossed area in Figure 7-1 1 confirmed the existence of gold in sample. Changing of the precipitation pH even in a small range (7.8-9.2) induces structural non-uniformities, the size of gold particles ranging in a large interval (3-12 nm). The same behavior was found for the catalysts supported on MgO or TiO₂. Another interesting observation in these experiments was related to the necessity to carry out experiments under air conditions. XPS spectra of the fresh and tested catalysts indicated no differences in the binding energies of Au₄f levels. TEM experiments also showed no differences between the fresh and tested catalysts. To clarify the fact that the support is active under air conditions and can be recycled, XPS measurements of samples treated with air were carried out. For such a purpose the samples were cooled in the preparation chamber at 203K, and treated with air. After that they were transferred in the measuring chamber collecting spectra at 243 K, 253K, 271K, and 303K.
Figure 7-1 TEM images and EDX analysis of Au/betaNH4* support.
Figure 7-2 shows the evolution of these spectra. For comparison, samples as prepared were measured as well. Spectra collected for the Au_{4f} level at temperatures below 273 K for the samples as prepared showed a full width at half maximum (FWHM) higher (4.16 eV) than that being fixed at the instrumental resolution (1.2 eV). For the sample treated with air the FWHM was even larger. As previously reported by Lee group, such a behavior is not unreasonable at such temperatures and was explained by a significant binding site inhomogeneity. In agreement with these authors the width of the XPS peak presumably reflects the various geometries where isolated Au atoms are bound. However, the peaks recorded at lower temperatures can be easily decomposed into two components one located at 89.1 eV, associated with isolated atoms and another at 85.6 eV, assigned to Au small particles. For the samples treated in air the ratio of the isolated/aggregated Au atoms is higher. Thus, this may allow us to speculate that the role of air in this reaction is to keep a continuous dispersion, avoiding agglomeration in large aggregates.

In summary, we have found that gold supported on betaNH_{4}^{+} catalyzes the intramolecular addition of carboxylic acid to alkynes leading to functionalized lactones. XPS confirmed the role of Au(III) species in such reactions, and gave evidences about the effect of air in preserving the dispersion of oxidated species. The efficiency of this system allowed reactions under mild heterogeneous conditions. The high gold catalyst activity would probably allow other catalytic formations of C-O or C-N bonds.
Figure 7-2 XPS spectra collected at different temperature.
CHAPTER 8 IN-SITU STUDY OF OZONE INTERACTION WITH AG-AL CATALYSTS: EVIDENCES OF THE NATURE OF THE ACTIVE SITES

This work is done as cooperation between Richards’ group and Prof. Vasile I. Parvulescu’s research group in Romania. We prepared the catalysts and did the TEM analysis and some other characterization. The catalytic part work was mainly done by Prof. Vasile I. Parvulescu’s research group.

*In-situ* study of ozone interaction with Ag-Al catalysts prepared via embedding of pre-synthesised silver colloids in a surfactant assisted alumina support provided evidences of the nature of the active sites of silver for total oxidation reactions.

While thermal destruction of chemicals at high temperatures is effective, it is not economically feasible. Chemical oxidation through the use of agents such as ozone, hydrogen peroxide, chlorine or chlorine dioxide generally overcomes these difficulties[215]. Additionally, ozone has recently received attention for total oxidation reactions.

Transition metal oxides, and especially manganese oxides, were used to promote VOC oxidative decomposition on the catalyst surface by atomic oxygen due to their ability to decompose ozone. The catalysts containing Ag were reported to exhibit a higher activity in the decomposition of ozone as compared with other oxides. The influence of the support and its acidity in ozone decomposition was examined by impregnating different loadings of silver on both microporous (H-Beta) and mesoporous (H-MCM-41) supports and the acidic materials was shown to exhibit a lower activity in decomposition.
of ozone. Recently, silver supported on SiO₂ was reported to be disrupted by ozone leading to supported small Ag oxide particles.

The aim of this study is to present a new route to generate stable supported silver catalysts under an ozone atmosphere and examine their behaviour in the oxidation of toluene.

8.1 Preparation of catalysts

Silver colloids were prepared by reducing AgNO₃ in aqueous solution. In a typical preparation, 0.294 g sodium citrate was added to 50 mL of 10 mM AgNO₃ aqueous solution in an ice bath. NaBH₄ (0.019g) was added to the solution at once with strong stirring and a black powder formed in solution, was filtered, and dried at room temperature in a vacuum oven. The catalysts were prepared from 98.5g aluminum butoxide (Al(OBu)₃) which was dissolved in isobutyl alcohol then the mixture 17.2 g Pluronic 84 ((EO)₉(PO)₉(EO)₉), as surfactant, previously dissolved in isobutyl alcohol, was added. The resulting mixture was then refluxed at 70 °C for 6 h, water was added and the refluxing was continued at 80 °C for 10 h, and at 100 °C for 20 h. The Ag colloid dissolved in water was added to this mixture under vigourous strong stirring resulting in samples containing 3 and 5 wt% Ag which were denoted as AlAg₃ and AlAg₅, respectively.

8.2 Characterization of catalysts

The Ag content was confirmed by ICP-AES analysis. The prepared catalysts were studied ex-situ by BET, XRD, TEM and XPS as well as in-situ under an oxygen-ozone atmosphere by DR-UV-Vis and DRIFTS. Ozone was generated with a Trio3gen Ozone
instrument and the concentration of ozone was 0.06% in a 75.5 mL/min flow of He. Time-on-stream experiments were carried out using a concentration of toluene of 50 ppmV for a total flow rate of 510 sccm. The concentration of ozone was 1000 ppm and was measured with an Ozone Monitor Model 460 M, Teledyne Instruments. The effluent gas was analysed by gas chromatography, using a GC-2014, Shimadzu with FID detector. A gas analyser (Ultramat 6, Siemens) was coupled on-line to monitor continuously the concentrations of CO₂ and CO resulting from toluene oxidation. The catalysts (200 mg Al₄Ag) were placed in a catalytic reactor in an oven which was heated at 80 °C.

Textural characterization indicated that these materials are mesoporous with a surface area higher than 400 m² g⁻¹ and a bimodal pore size distribution (pores of 3 and 6 nm). XRD patterns recorded at small angles did not indicate the presence of any mesoporous structural organization. The patterns shown in in Figure 8-1 correspond to the reflection planes of bulk Ag (2θ = 38.1 °, 44.3 °, 64.4 ° and 77.4 °) as well as of γ-alumina. Exposure to ozone caused no significant change in the XRD patterns although a small decrease in the silver features was observed. TEM confirmed the preservation of the nanometric size of the colloids after their incorporation in the alumina support and the mesoporous texture (Figure 8-2). From the TEM the silver particle size was found to be predominantly in the range 3-5 nm, irrespective of the metal loadings. The particle size measured with the Scherrer formula was of 22 nm.

XPS confirmed the presence of silver and the binding energy analysis showed the preservation of the Ag(0) state even after calcination. The binding energy of Ag 3d₅/₂ level was observed at 368.6 eV for both silver loadings which is typical for Ag(0).
In-situ DRIFTS studies were performed using fresh catalyst as the reference material. The presence of ozone led to a significant decrease in the bands assigned to surface hydroxyl and also of the remanent carbonate species resulted after the calcination of the catalysts. Silver is known to be passivated by both chemisorbed oxygen and hydroxyl and carbonate species under ambient conditions; however, in the presence of ozone these species are scavenged from the surface. Some surface hydroxyl remains even after this treatment with a new band found at 3732 cm$^{-1}$ which increases with time. This feature is thought to be due to perturbations in the remaining OH groups by ozone adsorption. This demonstrates that the initial step of the ozone activation prior to reaction of the hydrocarbon is essentially a cleaning of the surface. Similar changes are also found under thermal treatment in an inert gas environment; however, these changes are very
slow. The band at 3732 band was not observed under He, which means the final state of the catalyst is different under the two different atmospheres.

Figure 8-2 TEM picture of AlAg13.

Figure 8-3a shows DR-UV-Vis spectra collected at 30°C under helium and ozone. The main feature of the 3% Ag sample at 30°C under both helium and ozone is a band at 225 nm which is assigned to isolated Ag⁺ ions. No change in the band position was detected as a function of temperature under helium (Figure 8-3b). Under ozone the band at 225 nm increases in intensity and shifts to 218 nm on heating to 100°C (Figure 8-3c). Heating the 3% Ag sample under ozone shows no change in species but an increase in intensity of the band due to Ag⁺ species.
Figure 8-3 DRS-UV-Vis spectra of (a) 3% and 5% Ag/Al₂O₃ at 30°C under helium and ozone (0.06% O₃ in O₂); normalised to the most intense band in the spectrum. The 5% Ag/Al₂O₃ (grey line) shows an increase in Agₙ⁺⁺⁺ clusters under ozone at 30°C yet under helium the spectra resembles the 3% Ag/Al₂O₃ which is comparable under helium and ozone. (b) 3%Ag/Al₂O₃ under helium with increasing temperature and (c) 3%Ag/Al₂O₃ under ozone with increasing temperature. Spectra were recorded every 10 minutes.
The UV-DRS spectrum of the 5%Ag sample under helium at 30 °C is also dominated by a band at 225 nm; there is no effect of loading on the Ag species under Helium. However, at 30 °C under ozone, bands due to \( \text{Ag}_n^{5+} \) (260 nm) and large silver clusters (320 nm) are present. Under ozone, Ag species are changed compared to the fresh catalyst even at 30°C for this higher loading catalyst. On heating to 100°C under ozone, these bands are depleted and only \( \text{Ag}^+ \) ions are present as for the 3%Ag sample.

The higher loading affects the initial silver species but under ozone, it is \( \text{Ag}^+ \) species which are present at the reaction temperature of 80 °C irrespective of loading which indicates that \( \text{Ag}^+ \) species may be important and stable under an ozone feed compared to silver clusters or larger particles. It is noteworthy, that for the impregnated catalysts (also 3% loading of Ag), the interaction of Ag with ozone led to the redispersion of small clusters to \( \text{Ag}^+ \) ions, as has been observed for the colloid catalysts[216].

![Figure 8-4 Proposed model for the interaction of ozone with catalyst](image)

Based on data collected in this study we propose the interaction model given in Figure 8-4. This is essentially different from that described in the literature. It shows a first step representing a cleaning of the surface and a passivation to \( \text{Ag}^{5+} \) species (demonstrated by DRIFTS) and an accumulation of ozone demonstrated by DR-UV-Vis spectra. According to XPS and XRD results the core of the embedded silver colloids is constituted from Ag(0) species. The coverage of ozone exhibits no influence on the state of the silver particles.
Figure 8-5 shows the *in-situ* DRIFT spectra following treatment of the catalyst in a mixture of O$_3$ and toluene for the AlAg3 catalysts (3%Ag/Al$_2$O$_3$ impregnated). The adsorption of toluene at 80 °C on a cleaned surface leads to the appearance of a weak bands at 3028 cm$^{-1}$, 1604 and 1496 cm$^{-1}$. The band at 3028 cm$^{-1}$ is due to C-H stretch and the bands at 1604 cm$^{-1}$ and 1496 cm$^{-1}$ to ring stretching vibrations of adsorbed toluene. A negative band at 3745 cm$^{-1}$ is also observed which suggests that toluene adsorption is interacting with OH of alumina surface. As the temperature is increased to 300 °C, bands due to adsorbed toluene are depleted. On returning to 80 °C, adsorbed toluene is observed again. Upon introduction of ozone, bands due to toluene are depleted and new weak bands are evident and assigned to phenolate C=C stretching at 1590 cm$^{-1}$ (shoulder on 1604 cm$^{-1}$ ring stretching vibration) and between 1460 and 1430 cm$^{-1}$ and also a new band at 1300 cm$^{-1}$ which is assigned to the C-O stretching of phenolate.

No change in the oxidation state or size of the embedded colloids have been evidenced after several catalytic cycles proving that this preparation methodology is leading to very stable catalysts for the oxidation under harsh conditions using ozone. As mentioned above, impregnation is leading to precursor catalysts which after the exposure to ozone generate via a disruption mechanism active and non-active spectator species. This preparation procedure leads only to stable active species in which all the introduced silver participates at the catalytic reaction.
Figure 8-5 In situ O₃-toluene-DRIFT spectra on the AlAg3 catalyst. (a) 80°C in He, (b) 80°C + toluene, (c) 150°C + toluene, (d) 300°C + toluene, (e) 80°C + toluene + O₃. Spectra were recorded every 10 minutes.

Time on stream experiments made in oxidation of toluene with ozone on AlAg3 catalyst at 80°C showed a conversion of 83%. The only reaction product was carbon dioxide. These data demonstrate, indeed, a very high activity of these catalysts under rather small temperatures.

In summary, In-situ study of ozone interaction with Ag-Al catalysts prepared via embedding of pre-synthesised silver colloids in a surfactant assisted alumina support
provided evidences of the nature of the active sites of silver for total oxidation reactions.

Ozone is chemisorbed on embedded Ag colloidal catalysts without any change in the oxidation state and size. The population of the chemisorbed species is higher at lower temperatures, where the non-selective decomposition of ozone is smaller.
I have investigated the application of seed-mediated growth to form well-defined nanorods embedded in the channels of SBA-15. By using an appropriate synthetic approach, well-defined gold nanorods could be prepared in the SBA-15 channels and the length of gold nanorods could be tuned by changing the ratio of seed to gold precursor. The formation of gold nanorods and their relatively narrow size distribution were confirmed by both HAADF-STEM (High Angle Annular Dark Field Scanning Transmission Electron Microscopy) imaging and diffuse reflectance UV-VIS spectroscopy. Electron tomography was used to evaluate the 3-D distribution of the gold nanorods in the SBA-15 matrix. The results showed that the nanorods were well distributed within the channels, all roughly parallel to each other throughout the SBA-15 microcrystal. This makes the gold nanorods/SBA-15 composite an interesting material for optical and catalytic applications. The gold nanorods/SBA-15 composites can be treated as gold heterogeneously immobilized on silica. The catalytic units are well-defined gold nanorods with fixed diameter and tunable length which have a strong contact with the walls of the SBA-15 pores without blocking the open system of SBA-15 due to the existence of micropores perpendicular to the main pores in SBA-15 material. This makes them an ideal model to study the influence of shape and size of gold nanoparticles on their catalytic activity.[45] On the other hand, the gold nanorods/SBA-15 composite can also be treated as gold nanorods “suspended” in silica. Compared to the gold nanorods in liquid suspension, the gold nanorods “suspended” in silica have a much higher concentration and preferential orientation. High concentrations are required to obtain
strong signals for optical applications especially in ultra-sensitive medical imaging techniques.[218] The parallel orientation of gold nanorods in a SBA-15 microcrystal makes it possible to be used as a 3D polarizer.

9.1 Preparation of gold nanorods in SBA-15 channel

Figure 9-1 Synthesis scheme of in-situ growth of gold nanorods in the channels of SBA-15.

The synthetic approach used to prepare length tunable Au nanorods/SBA-15 composites is shown in (Figure 9-1). Gold nanoparticles, which are working as seeds for the following steps, were formed in the channels of SBA-15 by a simple impregnation method. Different amounts of gold precursor (Table 9-1) were used to grow the gold nanorods from same amount of seeds to obtain different lengths. Unsupported gold nanorods can be extracted by removing the silica matrix with 2% HF and 1% dodecanethiol as ligand.
9.1.1 Synthesis of APTES-modified SBA-15 mesoporous silica

Mesoporous SBA-15 was prepared as reported in the literature. [190] In a typical synthesis, 4g Pluronic123 (triblock copolymer from BASF, EO20.PO70.EO20) was dissolved in 120 ml 2M HCl at 40 °C under stirring. After fully dissolving the polymer, 0.041 mol TEOS was added, and stirring maintained for 24 hours at 40 °C. Then the solution was transferred into a teflon autoclave and kept for 3 days at 95 °C. Afterwards, the powder was filtered, dried and calcined at 550 °C for 8 hours, resulting in template-free SBA-15. To modify the surface, 2g of the prepared SBA-15 powder was suspended under stirring in 100 ml APTES ethanol solution (1 wt %) for 3 hours, and then carefully filtered, washed with ethanol and dried at 60 °C. The surface modified SBA-15 is marked as APTES-SBA-15 in this report.

9.1.2 Preparation of Au seeds immobilized in SBA-15 channels

The Au seeds immobilized in SBA-15 channels were prepared via an impregnation approach. In a typical experiment, 2g of APTES-SBA-15 powder was suspended in 200ml 1 mM HAuCl₄ (aq) solution and stirring maintained for 2 hours. Then the solid was filtered out and rinsed three times with deionized water. After calcination at 350°C for 3 hours, a light pink powder (the characteristic color of gold nanoparticles) was obtained (Seeds/APTES-SBA-15).

9.1.3 Growth of gold nanorods in SBA-15 channels

Gold nanorods were prepared by a modified seed-mediated growth method. Specifically, 0.1g Au seeds/SBA-15 powder was suspended in 100 ml of 0.1 M CTAB (aq) by stirring in an ultrasonic bath for 3 minutes. The well dispersed seeds/SBA-15...
slurry was important for the uniform growth of gold nanorods. 0.2mL of 0.01 M AgNO₃ aqueous solution, 0.2 ml of 0.067 M HAuCl₄ trihydrate (aq), and 0.14 ml of 0.1 M ascorbic acid (aq), were added consecutively, with continuous stirring. To ensure full formation of gold nanorods, 24 h reaction time was used, after which the solid powder was filtered from the mixture, rinsed three times with deionized water and ethanol to remove the CTAB and dried at 95°C. Finally, a red powder was obtained. This powder was marked as Rods100/SBA-15 (‘100’ indicates the relative ratio of gold precursor/seeds). Rods40/SBA-15 and Rods400/SBA-15 were prepared in the same way but with different ratios of gold precursor to seed in the growth solution (see Table 9-1 for details). With the increase of the gold precursor to seed ratio, the color of the final product varied from pink to gray. By removing the silica matrix with 2% HF and 1% dodecanethiol as ligand, unsupported gold nanorods were obtained.

Table 9-1 Preparation details of different sample.

<table>
<thead>
<tr>
<th>Seeds/SBA-15</th>
<th>0.1M CTAB (ml)</th>
<th>0.067M HAuCl₄ (ml)</th>
<th>0.01M AgNO₃ (ml)</th>
<th>0.1M Ascorbic acid (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rods100/SBA-15</td>
<td>0.1 g</td>
<td>100</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Rods40/SBA-15</td>
<td>0.1 g</td>
<td>100</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>Rods400/SBA-15</td>
<td>0.1 g</td>
<td>100</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>
9.2 Results and discussion

9.2.1 Liquid nitrogen adsorption and desorption

\( N_2 \)-Adsorption data (Table 9-2) showed decreased values in surface area, pore volume and mean pore size for APTES-SBA-15, Seeds/SBA-15, and all three Rods/SBA-15 samples as compared to their parent SBA-15 materials as expected due to the pore-filling effect.[219] However, only slight differences were found between the Seeds/SBA-15 sample and the three Rods/SBA-15 samples because the density of Au is much higher than \( \text{SiO}_2 \) and the total volume of the nanorods is no more than 1% of the total pore volume (calculated for a sample containing 6wt% gold), which implied the growth of nanorods did not block the open porous structure of SBA-15.

Table 9-2 \( N_2 \)-Adsorption data and length of nanorods in different samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m( ^2 )/g)(^a )</th>
<th>( V_{\text{BJH}} ) (cc/g)(^b )</th>
<th>( D_{\text{BJH}} ) (nm)(^b )</th>
<th>Length of rods (nm)(^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>613</td>
<td>0.899</td>
<td>4.89</td>
<td>/</td>
</tr>
<tr>
<td>APTES-SBA-15</td>
<td>436</td>
<td>0.721</td>
<td>4.88</td>
<td>/</td>
</tr>
<tr>
<td>Seeds/SBA-15</td>
<td>421</td>
<td>0.697</td>
<td>4.93</td>
<td>3-5 (spheres)</td>
</tr>
<tr>
<td>Rods40/SBA-15</td>
<td>400</td>
<td>0.662</td>
<td>4.88</td>
<td>20-30</td>
</tr>
<tr>
<td>Rods100/SBA-15</td>
<td>372</td>
<td>0.691</td>
<td>4.83</td>
<td>30-50</td>
</tr>
<tr>
<td>Rods400/SBA-15</td>
<td>410</td>
<td>0.654</td>
<td>5.53</td>
<td>100-200</td>
</tr>
</tbody>
</table>

\(^a\) The surface area \( S_{\text{BET}} \) is calculated by BET method. \(^b\) The pore volume and the pore size distribution are determined by the BJH model applied to the desorption branch of isotherm. \(^c\) The length of nanorods is determined by TEM.

9.2.2 The morphology of gold nanorods in SBA-15 channels
Figure 9-2 HAADF-STEM images of the A) Seeds/SBA-15, B) Rods100/SBA-15 (inset is a BF-TEM image at higher magnification), and BF-TEM images of C) unsupported Au rods after removing silica matrix and D) HR-TEM image of single-crystalline domain at unsupported Au rods (the inset shows the corresponding Fast Fourier transform of the area indicated).
To study the morphology of the Au nanorods embedded in SBA-15, HAADF-STEM imaging was used, as Z-contrast offers a better gold/silica contrast compared to BF-TEM. Figure 9-2A shows the HAADF-STEM image of Au seeds/SBA-15 prepared by impregnation method. In the Z-contrast images, the Au seeds appear as bright dots with a diameter of 3-5 nm in the pores of the SBA-15. The inset is STEM image of a SBA-15 particle with the orientation of [001] zone axis, which clearly shows the hexagonal pores. The average pore distance is measured to be 9.3 nm which corresponds to the sum of pore diameter and wall thickness.

After performing the seed-mediated growth process, gold nanorods were observed in the channels of SBA-15. Figure 9-2B shows an overview of Rods100/SBA-15 sample. Large amount of short gold nanorods (the bright rods, which were shown to be gold nanorods by EDX analysis, see Figure 9-3) embedded in a portion of SBA-15 with dimensions of about 1*3 μm were observed. Those short Au nanorods have a fairly uniform size and are oriented parallel to each other. From the BF-TEM inset of a thin edge of a SBA-15 particle, it can be clearly seen that the gold nanorods are oriented parallel to the channels in the SBA-15. The measured diameter of the gold nanorods is typically in the range of 6-7 nm which is 2-3 nm smaller than the average pore distance of SBA-15. This suggests that the gold nanorods are dominantly growing inside a single pore of the SBA-15. Nevertheless, depending on the crystallographic orientation of the SBA-15 in the individual (S)TEM image, it might appear as if the gold nanorods are actually bigger than the pores due to the projection of the hexagonal pore structure, e.g. close to the [110] or [210] zone axis orientation.
Figure 9-3 EDX analysis of Au Rods40/SBA-15. A significant gold signal was detected focusing on the nanorod in area “1”, whereas no gold signal was detected at the blank “2” zone.

Extraction of gold nanorods from mesoporous matrix is important for the application of nanorods as building blocks for nanodevices and allows further characterization. Here, the gold nanorods were extracted by etching the silica matrix with 2% HF. The Au nanorods extracted from Rods100/SBA-15 exhibit a uniform diameter around 6-7 nm and an average length of about 30-40 nm. The diameter of the gold nanorods is slightly higher than the size of SBA-15 pores due to the pore-filling effects. In addition to the Au nanorods, a few large particles can also be seen in Figure 9-2C. I
believed that those particles formed in solution rather than in the channels of SBA-15 and were physically absorbed on the external surface of the SBA-15 template. From the high magnification image (Figure 9-2D), one can see that the gold nanorods are crystalline and exhibit the characteristic lattice spacings of gold.

9.2.3 3D-reconstruction of Au nanorods in SBA-15 channels

Due to the limitations of 2D imaging, it is hard to judge how the nanoscale gold rods are distributed in the layers of the nanoscale channels of the SBA-15 microcrystals by traditional TEM. Electron tomography[220] (3D TEM) was used to visualize a SBA-15 particle around 0.4*0.4*0.4 µm including all gold nanorods embedded in it. In my experiment, electron tomographic data was obtained in HAADF-STEM mode using a single tilt holder to acquire 151 images over a tilt-range of -75 to 75 degrees. I use gold nanosphere (~5nm) as markers for alignment. IMOD (software) was used to align the tilt-series using a combination of cross-correlation and marker tracking. The 3D reconstruction was performed in Inspect3D using the SIRT algorithm with 25 iterations.

The digital slices through the reconstructed volume in Figure 9-4A show the ordered porous structure of the SBA-15 matrix with several nanorods embedded. The inset fast Fourier transform (FFT) image does not show the well known hexagonal symmetry of SBA-15[221] because the orientation is not exactly in the direction of pores. In the XY slice, a small angle around 30 degree can be observed between the direction of pores and X axis. After compensating the misorientation of this angle, the corrected FFT indicates that the distance between the centers of SBA-15 channels is around 9.57 which
is the sum of the diameter of pore and the thickness of the wall. However, the gold nanorods fit well in the channels in both XY and YZ slices.
Figure 9-4 Tomography visualization of Rods100/SBA-15. A) digital slices though the reconstructed volume (the inset is the fast Fourier transform of order porous structure of SBA-15) and B-F) overall visualization of the gold nanorods embedded in a small piece of SBA-15 viewed from different directions.

In the overall visualization of Au Rods100/SBA-15, the SBA-15 matrix is displayed as volume rendering in red and the gold nanorods are displayed as surface rendering in yellow. When observed from the view parallel to the SBA-15 channels (Figure 9-4B), only the sphere-like ends of the gold nanorods can be observed. With the rotation of the whole system around the Y axis (green) the uniform gold nanorods, 40-50 nm in length (Figure 9-4D), are found to be evenly distributed throughout the entire
SBA-15 portion. Several very short nanorods can also been found at the top, which I believe were absorbed on the external surface rather than formed in the channels of SBA-15. This electron tomography clearly shows that the uniform gold nanorods are evenly distribution throughout the SBA-15 support.

**9.2.4 The tunable length of Au nanorods in SBA-15 channels**

One of the advantages of using the seed-mediated growth method is the tunability of the aspect ratio by varying the ratio of seeds to gold precursor, which makes this method very attractive since the longitudinal plasmon wavelength of elongated nanostructures is strongly dependent on the aspect ratio. However, the diameter of the nanorods also increases with the aspect ratio in a typical seed-mediated growth process[13, 14]. Figure 9-5 shows the growth results in the channels of SBA-15 by using the same amount of seeds but various amount of gold precursor compared to the sample Rods100/SBA-15. The gold nanorods formed using 40% gold precursor (Rods40/SBA-15) were around 20-30 nm (Figure 9-5A), slightly shorter than in Rods100/SBA-15 (Figure 9-2B-D), while long nanorods (Rods400/SBA-15), typically around 200nm, were formed using 400% gold precursor (Figure 9-5B). However it is hard to judge the length of gold nanorods because of the influence of orientation which can be clearly seen from Figure 9-4B-F. No variation of the diameter of the gold nanorods was found during the length tuning. In Figure 9-5B, some parts of the nanorods are significantly thicker than other parts, which might be caused by the filling effects. The growth of the long gold nanorods expand the pores of SBA-15, partially breaking the wall where it is less solid and form some gold in adjacent pores. This also explains why the pore size of sample Rods400/SBA-15 are larger than its parent SBA-15(Table 9-2).
Figure 9-5 HAADF-STEM images of the A) Rods40/SBA-15 and B) Rods400/SBA-15. The insets are the BF-TEM images at higher magnification.

Figure 9-6 Diffuse-reflectance UV-vis spectra of Seeds/SBA-15 and Rods/SBA-15 samples with different length.

The optical properties of the Au/SBA-15 composites were studied by Diffuse-reflective UV/Vis (Figure 9-6). Seeds/SBA-15 showed a single surface plasmon
resonance peak at 526 nm. The nanorods/SBA-15 composites exhibited the same peak around 526 nm and, in addition, longitudinal plasmon resonance peaks were observed at 698 nm (Rods40/SBA-15) and 829 nm (Rods400/SBA-15). However, Rods400/SBA-15 showed only one peak around 520 nm. Because of their high aspect ratio of more than 20, the longitudinal plasmon peak is likely beyond the range of the instrumentation. Based on Mie’s theory, the plasmon resonances at 628nm and 828nm indicate gold nanorods with aspect ratios of around 3.5 and 5.5. Considering the fixed diameter of those gold nanorods, it can be estimated from the diffuse-reflective UV/Vis spectra that the nanorods in Rods40/SBA-15 and Rods100/SBA-15 have an average length of about 20-25nm and 30-40nm, respectively. The relative sharp longitudinal plasmon resonance peak in the spectrum of Rods40/SBA-15 indicates that the gold nanorods prepared using in-situ growth method have a relative uniform length distribution.

9.2.5 Factors influencing the growth of Au nanorods

Concentrated CTAB solution has been widely used in the seed-mediated growth of metallic nanorods due to its tendency to form elongated rod-like micellar structures[222] which are believed to play a role as a soft template in the growth process. Though I use a hard template in my work (the pores of SBA-15), the CTAB still played an important role in forming the gold nanorods with high aspect ratio and in controlling their aspect ratio distribution. In experiments performed out using the same procedures to prepare Rods 40/SBA-15 and Rods 100/SBA-15 but without CTAB, no gold nanorods were formed. The gold nanorods only formed after increasing the amount of gold precursor in the absence of CTAB and the nanorods formed were only about 1/10 to 1/5 of the length compared to the nanorods formed under the same conditions in the presence
of CTAB (see Figure 9-7). One of the possible obstacles to forming uniform gold nanorods in the SBA-15 matrix is the varying mass transfer resistance in the micrometer length channels which leads to different growth rates of gold seeds located at different depths within the channels. However this can be improved if the reducing agent is weak enough so that the reduction process becomes the limiting factor rather than the mass transfer. Ascorbic acid is a weak acid and a recent study shows that the presence of CTAB makes the reduction of the gold precursor a kinetically controlled process[223]. I believe that by the slow reduction of gold in the presence of CTAB, I could eliminate the influence of mass transfer and thus achieve a 3-dimensional uniform growth of the gold seeds embedded in different parts of the SBA-15 channels.

*Figure 9-7 BF-TEM image of Au nanorods/SBA-15 which was prepared (left) with the same procedure with Au Rods400/SBA-15 in the absence of CTAB (comparing with Figure 3C) and (right) with the same procedure with Au Rods100/SBA-15 in the absence of Ag(I) (comparing with Figure 9-2B).*

In addition to the importance of the CTAB in solution, the presence of Ag⁺ is also critical for the formation of gold nanorods and controlling their aspect ratios. For preparing Rods100/SBA-15 with average aspect ratio 5.5, the initial silver ion
concentration is 15% of the concentration of gold. In the final products, the concentration of silver is only 7% of the concentration of gold decided by ICP after digesting Rod100/SBA-15 by HF and aqua regia. This value is closed to the ratio of silver/gold in a typical SMG synthesis. However ICP measurement cannot distinguish between any silver in these samples that might exist as Ag0, Ag+, or AgBr on the nanorods surface or SBA-15 surface. In experiments without the assistance of Ag(I), the resulting gold nanorods showed a poor uniformity (see Figure 9-7). Besides the gold nanorods, notable amounts of undeveloped gold seeds were observed in the channels and over developed large rods were found at the surface. Ag(I) is known to significantly decrease the growth rate of gold nanorods[15], and I believe it helped to further reduce the effects of mass transfer limited synthesis.

9.2.6 Catalysis activity

The oxidation of benzyl alcohol was performed in the absence of solvent with 6 hours reaction time. No detectable benzene or toluene was produced in the reactions and the catalysis results are shown in Table 9-3. The gold nanorods in SBA-15 channels did not show any improved activity over the pure SBA-15 and their performance is even worse in term of selectivities. I believe the poor activities may come from the Cl\(^-\) and Br\(^-\) which are induced by using of HAuCl\(_4\) and CTAB which are widely believed to have a poisoning effect on gold catalysts.

However the gold nanorods/SBA-15 composite, with an open porous structure and length tunable catalyst center (gold nanorods), is a promising model to study the influence of shape on catalytic activity if the Cl\(^-\) and Br\(^-\) can be removed properly.
Table 9-3 Comparative data for solvent-free oxidation of benzyl alcohol. Results were obtained for the oxidation of benzyl alcohol after 6 hours of reaction. The oxidation was carried out by bubbling the oxygen into the reaction mixture (5 ml benzyl alcohol and 5 mg catalysts) at 100°C.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Conversion (mol.%)</th>
<th>Selectivity (mol. %)</th>
<th>Benzaldehyde</th>
<th>Benzyl benzoate</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>6.60</td>
<td>79.01</td>
<td>20.99</td>
<td></td>
</tr>
<tr>
<td>Seeds/SBA-15</td>
<td>8.03</td>
<td>52.88</td>
<td>47.12</td>
<td></td>
</tr>
<tr>
<td>Rods 100/SBA-15</td>
<td>6.35</td>
<td>67.99</td>
<td>32.01</td>
<td></td>
</tr>
<tr>
<td>Rods 400/SBA-15</td>
<td>8.87</td>
<td>54.87</td>
<td>45.13</td>
<td></td>
</tr>
</tbody>
</table>

9.2.7 Discussion

No special catalytic activities of gold nanorods were shown in the benzyl alcohol oxidation due to the poisoning effect of CTAB. However, the gold nanorods/mesoporous material system, as a highly tunable system (Figure 9-8) has a great potential in optical application.

1. The gold nanorods are parallel to each other due to the highly ordered-structure of mesoporous materials.

2. Gold nanorods are small enough (6-7 nm) in diameter to show the surface plasma resonance effect.

3. The diameter of gold nanorods (r) and transverse distance between adjacent gold nanorods (t) are decided by the pore size and wall thickness of mesoporous materials. Given the fact that the recent development in mesoporous material area both academically and industrially has offered hundreds mesoporous materials with various pore size and wall thickness (Table 1-4), those two parameters (r and t) are also tunable.
4. The lengths of gold nanorods are tunable as I demonstrate in my work.

5. The longitudinal distances between adjacent gold nanorods are decided by the distance of two adjacent gold seeds before applying the growth process. In theory, it could be tuned by the amount of gold precursor in the preparation of gold seeds.

Figure 9-8 The illustration of highly tunable gold nanorods/mesoporous material system for its optical application.
CHAPTER 10 SUMMARY AND CONCLUSION

In this work, I designed several catalysts and tested their activities using benzyl alcohol oxidation as a probe reaction. By correlating the activities to particle shape, the facet of support and contact interface I have developed a better fundamental understanding of gold heterogeneous catalysts. The main findings/conclusions from this work included:

I found a simple method to prepare uniform gold nanorods in the channels of mesoporous SBA-15. The prepared gold nanorods have a uniform diameter of 6-7 nm and a length tunable to 200 nm. My interest in this method lays not only in fabricating length tunable ultrafine gold nanorods but also in their potential application, especially as catalysts and optical materials. The high concentration of gold nanorods oriented parallel to each other within each SBA-15 microcrystal could be a good candidate to enhance the signal for optical applications of gold nanorods based on both polarized and non-polarized light. Due to the poisoning effect of Cl\textsuperscript{-} and Br\textsuperscript{-}, the gold nanorods in SBA-15 channels show no activity in the benzyl alcohol oxidation. However, the gold nanorods/SBA-15 composite, with an open porous structure and length tunable catalyst center (gold nanorods), is a promising model to study the influence of shape on catalytic activity if the Cl\textsuperscript{-} and Br\textsuperscript{-} can be removed properly.

I probed the influence of crystal structures of support MgO on the activity of Au/MgO catalysts by using benzyl alcohol oxidation as a probe reaction. Au/MgO(111) shows a significantly higher activity than the gold nanoparticles deposited on MgO(active) whose surface is dominated by (100) facet. Since the surface of MgO(111) nanosheets consists of pure oxygen atoms which are a good supply of electrons, the gold
nanoparticles sitting on the (111) surfaces are electron rich and more active than those deposited on (100) surfaces. The DFT calculation results supported my finding in experiments.

I found the simultaneous synthesis process can significantly increase the thermal stability of Au/Al₂O₃ by increasing the Au-Al₂O₃ interface. No agglomeration was found even after 5 hours calcination at 500 °C. Furthermore, the Au/Al₂O₃ prepared by this process shows a significantly better conversion at high temperature than that prepared by a typical wetness impregnation method. We attribute this to its excellent thermal stability.

I prepared gold catalysts on TiO₂@CeO₂ with high-efficient Ce⁺/Ce³⁺ redox couple. This catalyst is highly active in CO oxidation and heptanal oxidation.

Beside the works I mentioned above, I also did some works collaborating with Prof. Vasile I. Parvulescu’s research group in Romania to see the influence of gold chemical states. Those works show that the chemical state of gold is fundamental in cyclization.
REFERENCES CITED


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