T-3869

CATALYST PREPARATION AND EVALUATION FOR SYNTHESIS OF ANISOLE BY PHENOL ALKYLATION

by

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T-3869

A Thesis submitted to the Faculty and Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science (Chemical Engineering and Petroleum Refining).

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ABSTRACT

The objective of this thesis research program was to investigate the effect of catalyst formulation on the catalytic synthesis of anisole from phenol and methanol. The project was carried out in two phases, consisting of fabrication of experimental apparatus followed by catalyst testing and evaluation.

A flow reaction system consisting of a spinning-basket reactor and associated instrumentation was designed, constructed, and tested for this program. Evaluation and validation of the reactor system with respect to operation was carried out using methanol dehydration reaction as the test reaction.

Both acidic and basic catalysts were tested during the catalyst evaluation portion of this program. The acid catalysts tested were the Lewis acid (γ-alumina) and Brönsted acid (phosphated alumina) type, while the base catalyst consisted of Na_2HPO_4 impregnated on a silica support. Activity and selectivity of these catalysts was evaluated in a temperature range of 250 to 350° C at a weight-hour-space-velocity of 5 hr^{-1}. In general, the acidic catalysts were found to be more active but less selective than the basic catalysts. Maximum selectivities found for formation of anisole for the Lewis and Brönsted acid catalysts were 10 and 32% respectively, while the maximum selectivity of the basic catalyst was 94%. Addition of phosphorus to γ-alumina was found to inhibit the formation of high alkylated phenols as side reaction. Stability testing of the basic catalyst indicated that deactivation became significant at a temperature of 400° C.

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ACKNOWLEDGEMENTS

The author would like to express his sincere thanks and appreciation to Dr. Robert Baldwin for funding this research and providing invaluable advices and suggestions throughout this thesis project.

Thanks and appreciation are extended to Dr. Scott Cowley for his guidance and advices and for serving as a thesis co-advisor.

Finally, the author gratefully acknowledges the financial support provided by Saudi Aramco to pursuing graduate study.

I. INTRODUCTION

Addition of oxygenated compounds to motor gasoline has been hailed recently as one of the more effective means of reducing atmospheric pollution caused by automobile emissions. Methanol, ethanol, and aliphatic ethers (e.g. MTBE) have all been proposed and used in various applications around the U.S., with varying degrees of success. One class of oxygenated fuels that has not received much attention to date is the methyl aryl ether (MAE) family, consisting of oxygenated aromatics such as methoxy benzene (anisole). These compounds have been tested as potential additives for motor fuel, and have been found to be highly compatible with normal unleaded gasoline. Engine performance and driveability were found not to be effected by additions of methyl aryl ethers (MAE's) up to a level of 15 volume percent, in contrast to the significant problems often encountered where other oxygenated additives are concerned.

The major problem blocking utilization of MAE's as an oxygenated fuels additive has been the high cost associated with manufacture of these materials. Recently however, the potential availability of large quantities of inexpensive phenols as a by-product from coal pyrolysis and or coal gasification tar streams has led to a re-examination of alternate synthesis route for MAE's, utilizing phenol as one of the starting materials. Very little research has been carried out on this process, as indicated by the paucity of public and patent literature on this reaction.

Oxygenated Fuels: Atmospheric pollution caused by emissions from automobile is one of the most serious problems faced by many metropolitan areas in the United States today. With the advent of the catalytic converter, many of the more troublesome emissions were greatly reduced, but due to the massive nature of the source, atmospheric phe-

nomena (e.g. temperature inversion) and other non-associated effects many of the more densely populated cities in the U.S. still experience severe incidents of smog on a regular basis.

Several techniques have been employed in an attempt to improve air quality, including mandatory no-drive days, and alteration of engines, and more recently, changes in the fuel itself. Addition of oxygen-containing compounds such as methanol and ethanol has long been touted as one approach to achieving a partial solution to environmental problems by means of fuel modification. Within narrow volumetric addition limits, both methanol and ethanol are compatible with gasoline. Ethers such as methl-tertiary butyl ether (MTBE) which are generally derived from petroleum by-products have also been employed for the same purposes. Since all of these components carry oxygen into the combustion cycle along with the hydrocarbon fuel, the engine can run leaner hence reducing the concomitant emissions. One of the most difficult pollutants to reduce and control is carbon monoxide. Use of oxygenated fuels has been shown to be a very effective means of achieving rather dramatic reductions in CO emissions from automobile engines. The overall effects of air/fuel ratio on emissions of CO and unburned hydrocarbons (HC) is well known, with both carbon monoxide and unburned hydrocarbons dropping rapidly as the air/fuel mixture becomes leaner. The efficiency of oxygenates in reducing automobile emissions, especially CO, has recently been tested on a very large scale in metropolitan Denver, where carbon monoxide is often the pollutant present in the largest amount during the winter months. Mandatory addition of up to 10 volume percent oxygenates in motor gasoline was legislated for metro Denver during the winter of 1988, and other cities such as Los Angeles are now considering similar measures.

While both methanol and ethanol have reasonably good combustion properties, nei-

ther are ideal oxygenated additives for gasoline. The blending octane values of methanol and ethanol at 10 volume percent are 115 and 118 (research+motor/2) which imparts the added benefited of octane enhancement to these materials. Methanol + gasoline blends have a very high Reid vapor pressure which leads to vapor lock and hence limits the utility of this material as a gasoline additive especially during hot weather. Additionally, methanol will separate when blended with gasoline if water is present in the fuel system, and is corrosive and incompatible with many of the elastomeric materials present in automobile fuel systems. While ethanol has a much lower Reid vapor pressure (11 psi), it is expensive to produce and only small amounts may be added to gasoline before engine performance and driveability of most cars with normally-aspirated engine is experienced. Ethers such as MTBE also have very high blending octane numbers, and have acceptable low Reid vapor pressures (9 psi). These compounds have the additional advantage of being able to be produced from iso-olefins separated from refinery by-product stream; for example MTBE is usually produced by reaction of isobutylene with methanol.

Methyl Aryl Ethers: Aromatic ethers such as anisole and its various alkyl-derivatives would be ideal oxygenated additives for high-octane gasoline. Being aromatic in nature, these material are highly compatible with gasoline being produced today.

The objective of this thesis project was to investigate the synthesis of anisole from phenol and methanol and to study the effect of catalyst composition on the activity and selectivity for formation of this compound.

II. LITERATURE SURVEY

The reaction for production of anisole from phenol and methanol has not been investigated extensively.

Kotanigawa et al., 1971, studied the methylation of phenol over metal oxides catalysts to produce ortho-phenols such as o-cresol, 2,6-xylenol and 2,4,6-trimethylphenol. The reaction in this study was carried out at 350°C and atmospheric pressure in tubular flow reactor over MO-Fe_2O_3 catalysts containing Cu, Mg, Ca, Ba, Zn, Mn, Co or Ni each as M. It was found in this study that gasification of methanol took place simultaneously as a side reaction. From the relation between methylation and gasification, the activity of the catalysts was found to be in the following order: Cu > Zn > Ba > Ca > Co > Mn > Mg > Ni. These catalysts were prepared by the co-precipitation technique. The authors primarily wanted to show that 2,6-xylenol can be manufactured not only by metal oxide catalysts but can be also produced selectively.

Hattori et al., 1976, have studied two catalysts; magnesium oxide and magnesium oxide from carbonate hydroxide to investigate ortho-alkylation of phenol with methanol. These two catalysts were tested at 500°C and atmospheric pressure in a tubular flow reactor. These catalysts were found to be very selective in producing o-cresol. The selectivity was found to be 98% for (I) and 73% for (II) where o-cresol was produced more than 2,6-xylenol.

Nozaki et al., 1977, has tested six catalysts in a tubular flow reactor at 460°C and atmospheric pressure. Molar ratio of the feed was 2:1 methanol to phenol. These catalysts were: $Ca_3(PO_4)_2$, $CaHPO_4$, $Ca(H_2PO_4)_2$, BPO_4, CaO and MgO. $CaHPO_4$ and BPO_4 have been found to have selectivities of 19.0% and 25.4% in producing anisole.

Other catalysts had selectivities less than 2.0%. Ca_3PO_4 was shown to have a very high activity for ortho-methylation. These catalysts were also tested at different temperature and space velocities, and ortho methylation was found to be a maximum at 460° C. Anisole was the favored reaction at lower temperatures. The calcination temperature was also tested and found to have no major effect on conversion or selectivity. The authors have proposed the following mechanism:

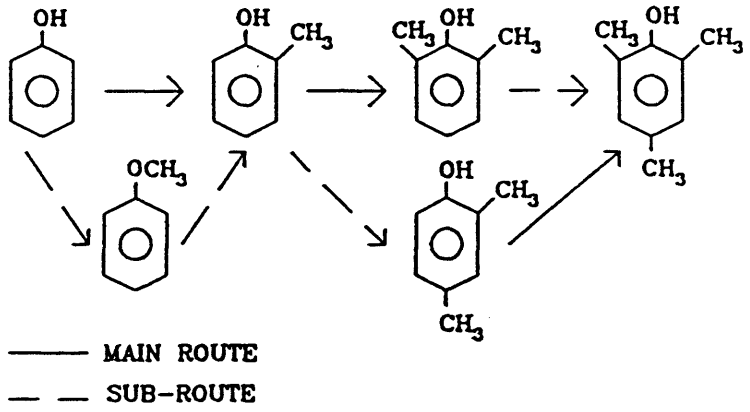


Figure 1: Proposed Mechanism by Nozaki et al., 1977.

Churkin et al., 1985, developed a kinetic model of phenol alkylation by methanol on a zeolite catalyst in a tubular flow reactor. At the lowest space velocity tested, the anisole yield did not exceed 7% at 300° C. This work by Churkin is part of a Russian patent and further details were not given.

Ionescu et al., 1987, conducted a study of phenol alkylation over a gamma alumina catalyst using operating conditions similar to those used by Nozaki et al.. Ionescu and his co-workers have focused primarily on developing a Langmuir-Hinshelwood mechanism rather than looking into the activity or selectively of this reaction. At a WHSV of 5, Phenol conversion was found to be a maximum. Lower space velocities were not tested. Ionescu et al., proposed the following mechanism:

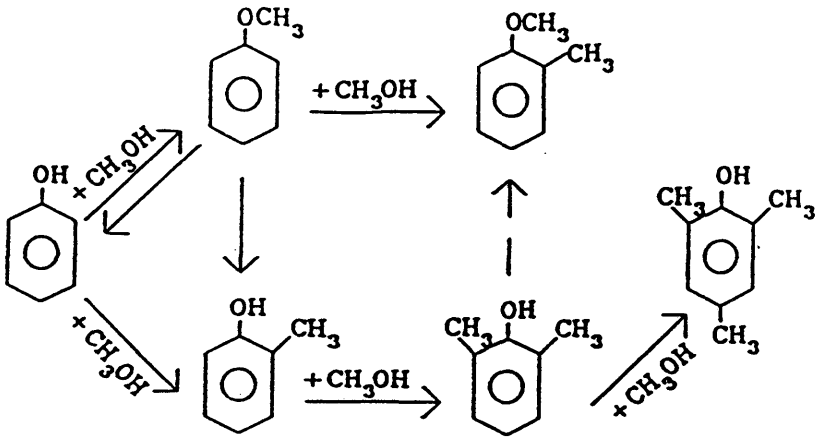


Figure 2: Proposed Mechanism by Ionescu et al., 1987.

Phosphate as a catalyst promoter: Phosphate has been investigated and recommended for use as a promoter for the following reactions: dehydration of alcohols , reforming, hydrocracking, catalytic cracking, and hydroprocessing (Moffat, 1978; Cull, 1980). Phosphate has been long used as an aid in the stability of the alumina support. Information relative to discoveries and observations for use of phosphate as a stability enhancer appears in the patent literature. Enhanced catalyst stability has been observed by Stirtion (1948) when he found the Co and Mo catalyst on alumina-aluminum phosphate exhibited high thermal stability and mechanical strength. Several investigators have reported on the use of phosphate to control pore size and distributions (Maholland, 1987).

Anisole as Fuel Additive: In 1980, Singerman of the Gulf Research and Development Co. published data which compared the properties of a blend of 5% anisole and unleaded gasoline in terms of engine performance, fuel economy, emissions, and other driveability and compatibility factors. The analytical results of this study are summarized in Tables 1 and 2, where data comparing these two fuels are shown. Essentially, no dif-

ferences in terms of fuel quality (except for an increase in octane number) were found between unleaded gasoline and the 5% MAE blend. Evidence that MAE's have octane enhancing characteristics is presented in Table 1.

Table 1: Research and Motor Octane Values for Base Gasoline and Base Plus Anisole

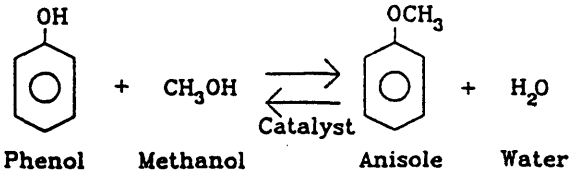
Gasoline	RON	MON
Base	93.2	84.1
Base + 5% anisole	93.8	84.5
Base + 10% anisole	95.4	85
Base + 15% anisole	96.3	85.4

Tests on the 5% anisole blend with plastics compatibility, toxicity, robistatic properties, deposit and gum formation, driveability, and fuel economy all indicated that no significant differences existed between the performance properties of automobiles using the blend vs. unleaded gasoline. In addition, it was found that the MAE's did not separate from gasoline at low temperature, or because of water contamination which can be a significant problem for gasoline/methanol blends.

Table 2: Properties of Base Gasoline and Base Plus anisole

Property	Base	Base + 5% anisole
Gravity (API)	56.8	53.7
Viscosity (cm)	0.56	0.57
Vapor Pressure (psi)	10.6	9.9
Alkalinity (pH)	5	5
Gum (mg/100ml)	1	1
Oxi. Stab. (min)	1440	1440

Aromatic ethers such as anisole can be synthesized in the laboratory (Willlamson synthesis) or, alternatively, MAE's can be produced by reaction of phenol with methanol:



Both methods of manufacture are not optimal in terms of production of MAE's. The former route is very selective but complex and costly. The literature on the catalytic reaction of phenol with methanol to form anisole is somewhat limited and indicates that both yield and selectivity problems exist with this synthesis route as it is currently practiced. In both cases, the cost of phenol as one of the major starting materials presents a significant economic barrier to utilization of these compounds as gasoline additives. Industrial techniques for manufacture of high purity phenol usually rely on complex and costly schemes involving either hydrolysis of aromatic diazonium salts (such as chlorobenzenediazonium hydrogen sulfate) or alkali fusion of synthesized aromatic sulfonate (e.g sodium p-toluenesulfonate). As a result, these types of compounds have not generated much interest to date as oxygenated fuels additives due to their high cost of manufacture.

Methanol Dehydration Reaction: This reaction has been studied by Schmitz et al., (1978), Garg et al., (1985), Brake, (1986), Kurpak et al., (1988), and others.

Cowley et al., (1988), studied this reaction in order to investigate a new concept for solving the methanol vehicle cold start and cold operation problem. The concept involved the on-board dehydration of methanol to produce highly volatile dimethyl ether. The dimethyl ether would be metered to the engine to assist with cold starting and cold operation. Four methanol dehydration catalysts were tested: silica-alumina, γ-alumina,

phosphoric acid treated γ-alumina, and fluorinated γ-alumina. The test was carried out in a micro catalytic plug flow reactor over a temperature of 200 - 350° C. Figure 3 presents Cowley's proposed mechanism for dimethyl ether formation over Lewis Acid Sites. Methanol is first dissociatively adsorbed on the hydrated surface, forming adsorbed methoxy groups and adsorbed hydroxyl groups. The adjacent methoxy groups then combine to form dimethyl ether and desorb from the surface. In the same fashion, the adjacent hydroxyl groups combine to water and desorb from the surface. The results of Cowley et al., (1988), were utilized to validate the catalytic CSTR operation designed in this thesis project.

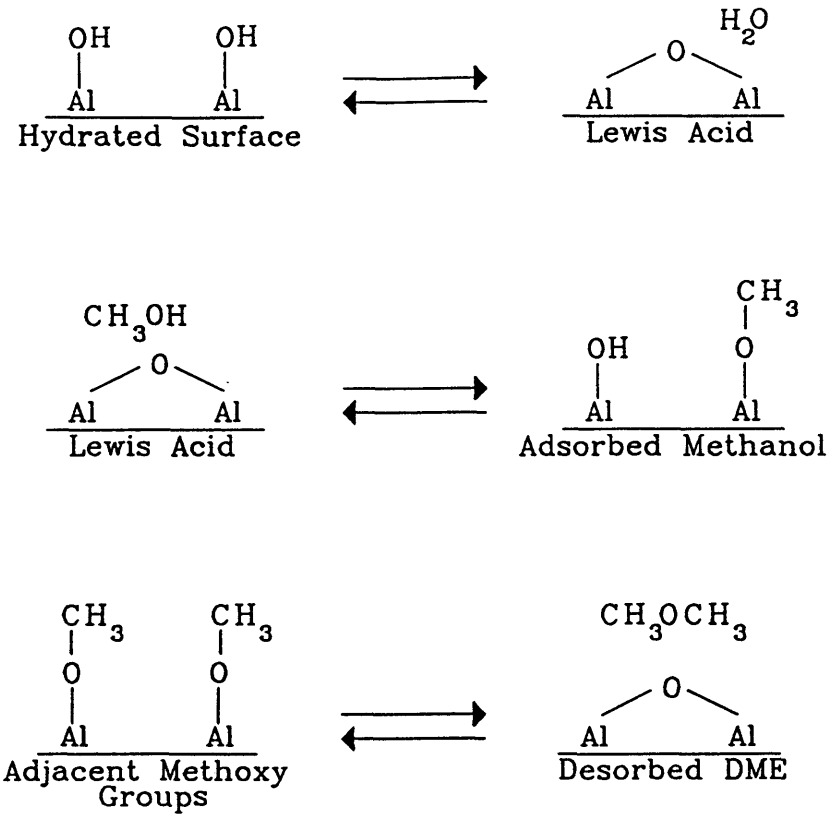


Figure 3. Proposed Surface Mechanism for DME Formation over Lewis-Acid Catalyst.

III. RESEARCH OBJECTIVES

The first objective was to design a catalytic CSTR which was capable of providing:

1. a high agitation rate to ensure perfect mixing,
2. a reasonably large quantity of catalyst permitting a wide range of WHSV.

Upon the completion of the design and construction of the experimental apparatus, the reactor was then validated by reproducing data in the literature on the dehydration of methanol. An ancillary goal at this stage of the program was to investigate the effect of particle size and stirring rate on intra and inter-particles mass transfer using the methanol dehydration test reaction .

The second objective was to study the synthesis of anisole via alkylation of phenol with methanol. Both acid-and base-catalysts were considered for this investigation.

IV. EXPERIMENTAL

IV.1 The "Ideal" laboratory Reactor

An ideal laboratory reactor is one which can be operated isothermally over a wide. range of conversions in the steady state with respect to the catalyst and reactants under clearly defined residence time conditions. The well stirred continuous flow reactor (CSTR), in principle, possesses many of these ideal characteristics (Carberry, 1964).

The CSTR has been used in large numbers of studies of reaction kinetics because it has the following advantages:

(a) It permits the study of kinetics without any complicating control of the reaction rate by gas-solid mass or heat transfer which are encountered in a packed bed reactor. These processes often intrude upon the surface reaction tending to falsify the rate data.

(b) It operates at a "perfect mixing" condition so that the bulk fluid temperature and concentration gradients are eliminated.

(c) It minimizes the temperature and concentration gradients between the bulk fluid and the catalyst surface.

(d) It can study all but the fastest and most exothermic reactions at nearly isothermal conditions and nearly complete conversion.

(e) Rates can be easily and accurately determined directly from the material balance equation.

Therefore, high agitation rate is a major requirement in designing an ideal CSTR. For this reason, the mixer speed is very crucial and careful mechanical design must be considered.

A widely used type of laboratory catalyst test reactor is a CSTR of the spinning-

basket type. This reactor was originally developed by Carberry and his co-workers at Notre Dame University. Carberry (1965) has given detailed mathematical derivation of the continuity equation where he has shown the effect of each rate processes on the chemical reaction.

Tajbl, Simson, and Carberry (1966) have studied the palladium-catalyzed oxidation of CO with O_2 and have documented results verifying the effectiveness of a catalytic CSTR for a study of heterogeneous reaction system. Reaction rates at different RPM's, 1 atmospheric total pressure and 220 - 234° C were determined. At a RPM of 1600, perfect mixing was found to prevail.

Tajbl, 1969, in later work studied the hydrogenolysis of ethane and propane over a commercial ruthenium catalyst in a spinning-basket CSTR. In this work the author discussed the significance of perfect mixing for determining the reaction rate and how to eliminate the interfacial effects. Tajbl has indicated that at a RPM of 2000, the interfacial effects were negligible and the gas solid contact was excellent.

Choudhary and Doraiswamy, 1972, have conducted a series of tests on one rotating basket CSTR and two stationary basket reactors. Mass transfer coefficients at different RPM's were determined using naphthalene evaporation as the experimental system. Perfect mixing was achieved with all reactors. The effect of gas flow rate on the mass transfer coefficient was also observed to be negligible except at very low stirring speed.

IV.2 CSTR Design and Construction:

To come up with an adequate design of the spinning-basket CSTR to be used in this study, the following factors had to be considered:

1. Maximum catalyst loading,
2. Gas/solid contacting,
3. High agitation rate of the reaction mixture,
4. Stable temperature and pressure control.

The foregoing considerations will be covered in detail in the following sections.

IV.2.1. Process and Equipment:

A process flow diagram of the experimental apparatus is shown in Figure 3. The feed flows from a glass burette (50 ml capacity) to a HPLC pump(Eldex A-30-S). The feed is then pumped through a preheater (SS, 1/8 inch ID, and 20 inch long wound in a cylinder coil of 2 inches diameter) and through a heat-traced (1/8" tubing, 316 SS) to the reactor. The products then flow through a heat traced product line (1/8" tubing, 316 SS) to a let-down valve (Whitey 316SS-21RS2, with graphite packing) where the reactor pressure is controlled. Past this valve the product goes through the first stage cooling (air-cooling) and then to the second stage (ice-bath condenser, 50 cc packed with stainless steel sponge) cooling and finally to the sampling valve (Whitey 316 SSOKS2). At this point the products are collected and retained for subsequent injection into the GC for analysis.

The pressure was controlled by the let-down valve. This valve is a high pressure and high temperature needle valve where the flow can be adjusted precisely. The product line upstream of the let-down valve is heat-traced to ensure that products do not condense

in the valve. This system provided very good control on the reactor pressure.

The temperature was controlled by a PI controller (Leed & Northrup Model) on the electric heater. A proportional gain, K_c ,of 1.0 and integral time constant T_I of 2.0 minutes were used. These tuning parameters provided excellent response with minimal damping and almost zero overshoot.

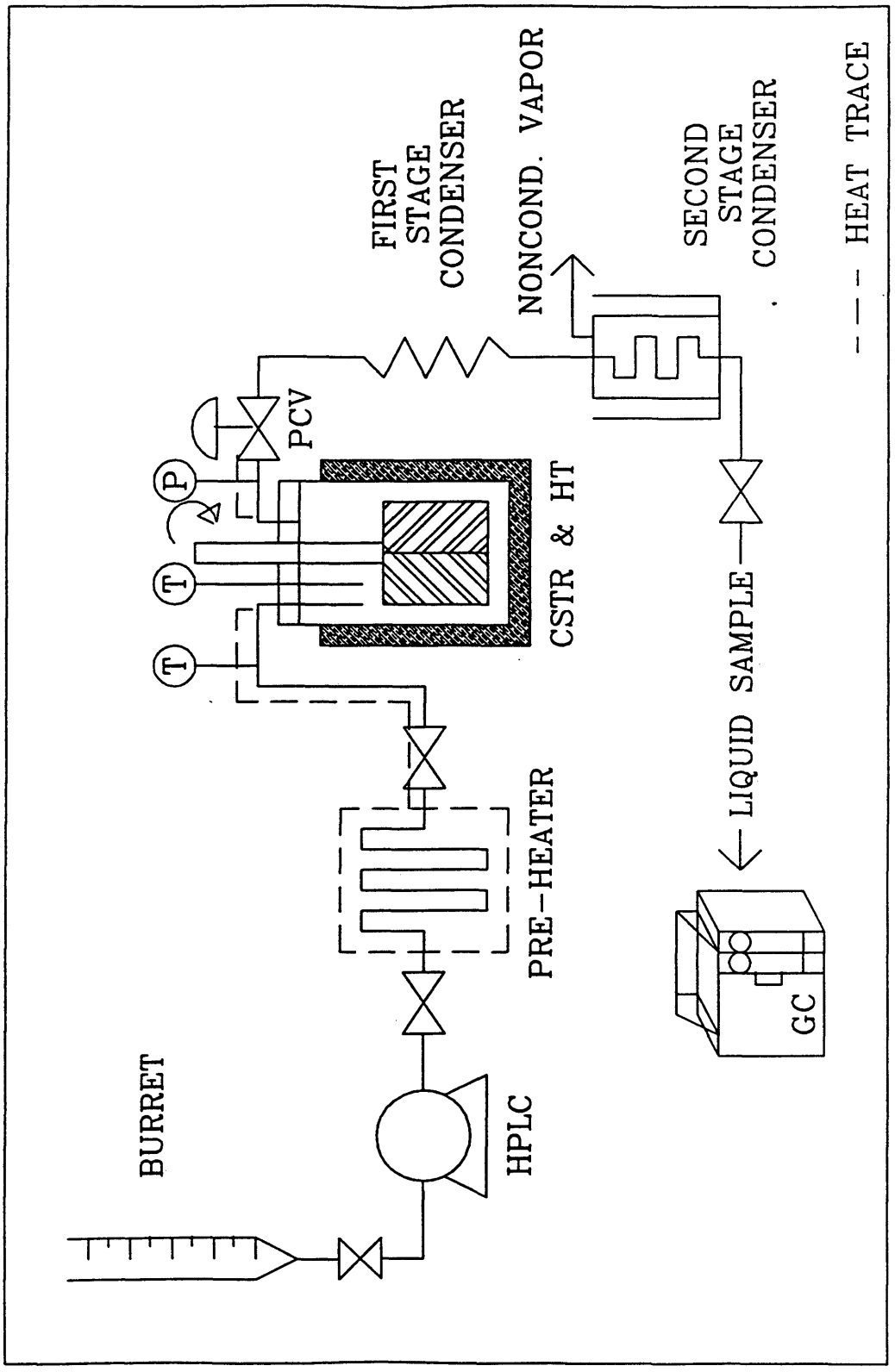


Figure 4. Process Flow Diagram for the Experimental Apparatus.

IV.2.2. Mechanical Construction:

The reactor used was constructed from a 300 cc Magnedrive packless Autoclave reactor (Autoclave Engineers). The reactor material is made of 316 SS. The reactor has an internal diameter of 1.8 inches and a height of 6.125 inches. The catalyst basket was fabricated from 304 SS by Karl Danninger of Golden,Colorado. A three dimensional sketch of the basket is shown in Figure 5. The four sides of the basket were mounted 90 degrees from each other by allen head screws (socket head cup screws). No welding was applied to the basket, thus eliminating any potential of materials failure which is typically associated with welding. The body of the basket is mounted to the shaft by a male screw extended from the basket body. This main screw has an internal shoulder where the basket can sit rather than sitting on threads. In this fashion the basket will not oscillate at high RPM. The basket was tested in Karl Danninger's shop at 1000 RPM and was found to exhibit no oscillation. The whole assembly was tested together in the laboratory at 2000 RPM and no oscillation was observed. Each side of the basket frame was equipped with an outside screen frame (14 mesh) which was held to the basket frame by allen head screws. If catalyst particles less than 14 mesh were to be used, another screen mesh with smaller mesh size can be fitted to the outside screen to prevent any catalyst losses. Detailed dimensions of the basket, and the reactors internals are shown in Figures 5 and 6.

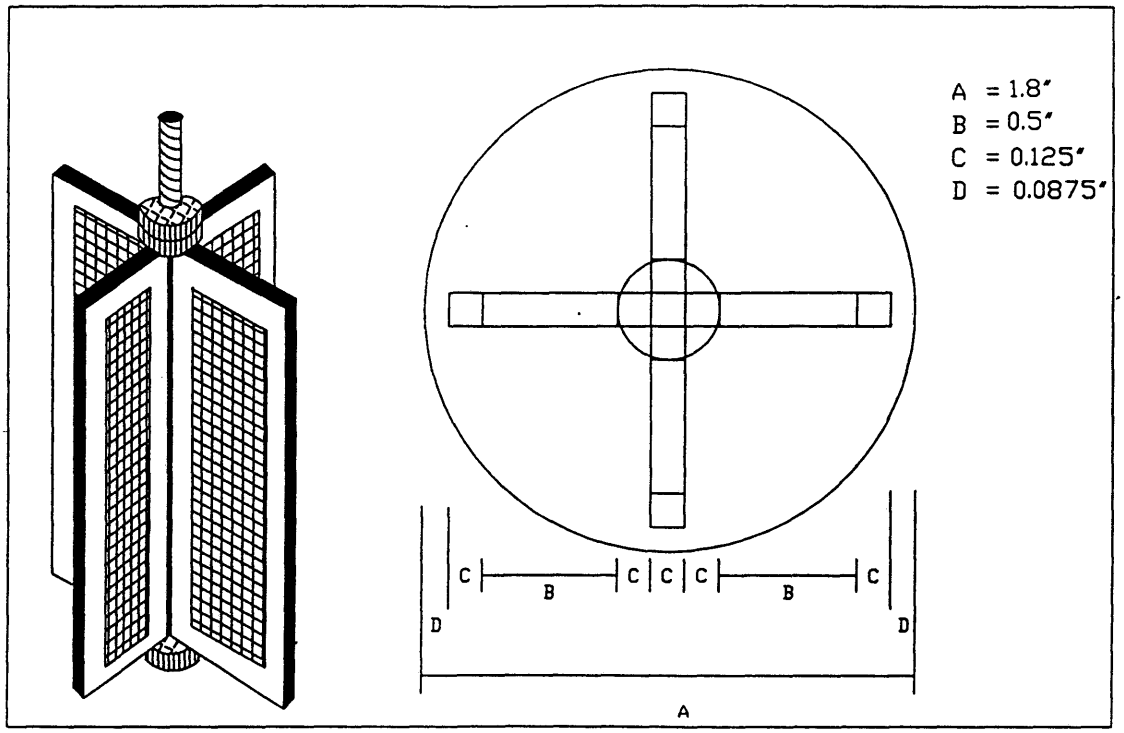


Figure 5. Detailed Dimensions of the Reactor Internals.

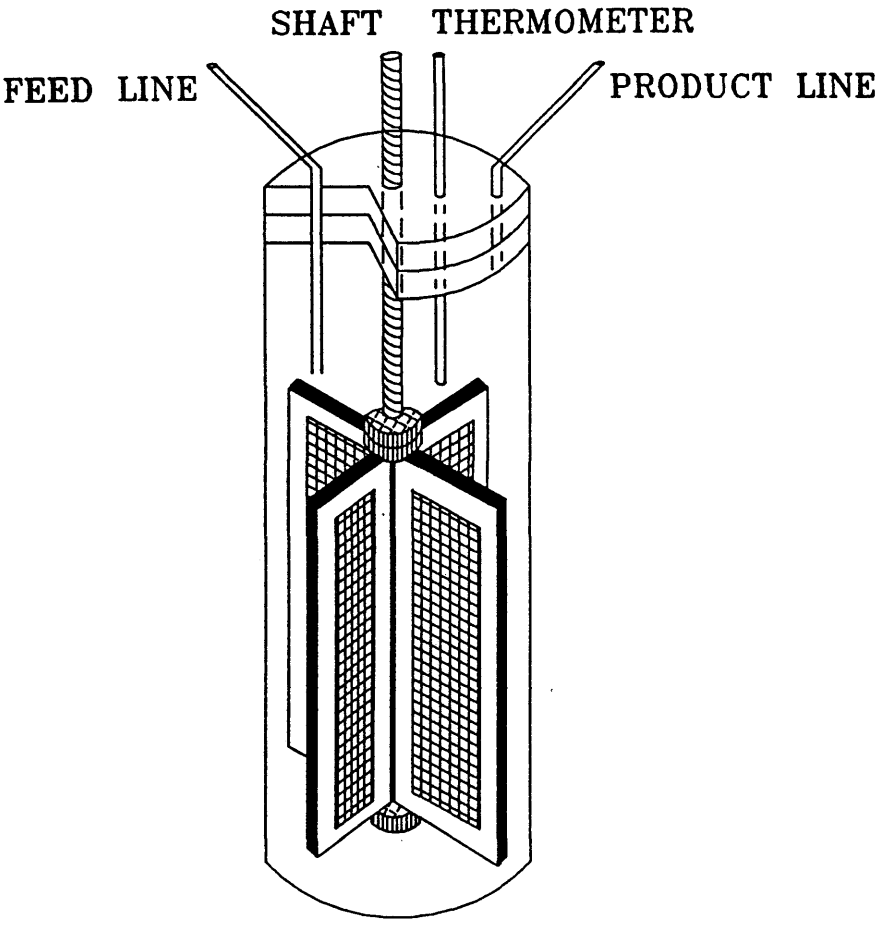


Figure 6. Cross-sectional View of the Reactor Internals.

IV.3 Experimental Methods :

IV.3.1. Catalyst Preparation:

The γ-alumina catalyst pellets used were supplied by Alfa Products (Morton Thiocal Company) and consisted of 99% aluminum oxide (3.2 mm pellets). The phosphated alumina catalysts used were provided by Dr. Scott Cowley of the CSM Chemistry Department, and were prepared by a co-precipitation technique. The preparation procedure is documented by Maholland (1987).

Base catalysts consisting of 10 % Na_2HPO_4 and 20 % Na_2HPO_4 were prepared by impregnating Na_2HPO_4 onto a commercial silica support (Davison # 57, surface area of 300 m^2/gm, pore volume of 1.0 cc/gm, and packed density of 0.4 gm/cc). 15 grams of the 14-20 mesh support was used each time. The support was first dried for 12 hours at 120° C and then calcined at 500° C for 12 hours. The calcined support was then left to cool for about half an hour and placed into a 250 ml round bottom 3-neck flask and evacuated using a water aspirator. Under vacuum, 13.5 ml of the impregnating solution was added to the flask. This addition of the impregnating solution was done very rapidly and was followed immediately by vigorous shaking of the flask contents to ensure uniform wetting of the support. The support was then taken out and dried for 12 hours at 120° C. The drying step had to precede the calcination because a high evaporation rate at high temperature will fracture the pores. After the drying step was finished, the catalyst was calcined for 12 hours at 500° C.

IV.3.2. Experimental Procedure:

The following procedure was followed for every run:

a. The reactor was cleaned and flushed with methanol before assembly.

b. The basket body and screens were cleaned very carefully to ensure that no carbon was left over from the previous run.

c. Catalyst is loaded on each side of the basket equally using the wooden saddle to hold the basket. Every side of the basket was then covered by stainless steel screen to prevent catalyst losses. Manual shaking of the basket will give an idea if this step has been done properly. This step is very important because escaping catalyst will plug the let-down valve and result in experiment shut down.

d. When catalyst loading is over, the catalyst basket is carefully screwed to the shaft. Manual tightening is sufficient. Over tightening is to be avoided.

e. The reactor is then ready for assembly. Care should be paid during the assembly because the clearance is very small.

f. The reactor top is then bolted down. Anti-sieze compound is applied to the reactor head bolts. Bolt tightening is done in a crossing fashion e.g 1,4,2,5,3,6. Tightening done first at torque of 30 Lb_f and then at the ultimate torque of 50 Lb_f.

g. After assembling all parts, the system is ready for leak test. Leak test is done using the helium gas connected to the experiment. The system can be pressurized up to 180 psig. Snoop liquid is used to check for the leaks. The system is then sealed and left to at over-night.

h. If the system shows no leaks after setting all night, then it is ready for startup. the system can be depressurized through the vent line. Heating up the system to startup should

be done very slowly (100 degree every hour).

i. The primary safety concern in this experiment is the hydrogen used as carrier gas for the Varian 3700 GC. The hydrogen cylinder must be checked for leaks. The GC columns must be checked for leaks too.

j. When temperature and flow rate have stabilized at the desired values, check for a steady-state by comparing: a) results of consecutive sample analyses on the GC; b) mass balance closures over 10 minute time intervals.

IV.3.3 Analytical Methods:

The analytical technique used to determine the product distribution was gas chromatography (GC). The GC used was a Varian 3700 equipped with a thermal conductivity detector. The column used to analyze for the methanol dehydration reaction was a column packed by the author at CSM. The column was 6 feet long and ID of 1/8" SS, packed with Porapak T polymers (-80+100 mesh). The other column used for analysis in the anisole synthesis study was a 15 meter high performance crosslinked methyl silicone megabore column. Hydrogen was used as a carrier gas in order to increase sensitivity.

In each case the column is first conditioned for two hours at the operating temperature and then followed by GC calibration. Tables 3 and 4 list the GC run parameters which were used throughout this study. Tables 14 and 15 in Appendix 1 represent the GC calibration results. Response factors were calculated as the average of multiple injections (at least 5 runs for each calibration mixture).

Table 3

VARIAN 3700 GC Run Parameters

Methanol Dehydration Reaction (Porapak T Column)

Temperature (°C / Isothermal)	150
Injector Temperature (°C)	200
Detector Temperature (°C)	250
Detector Current (mA)	273
Carrier Gas Flow Rate (cc/min.)	30

Table 4

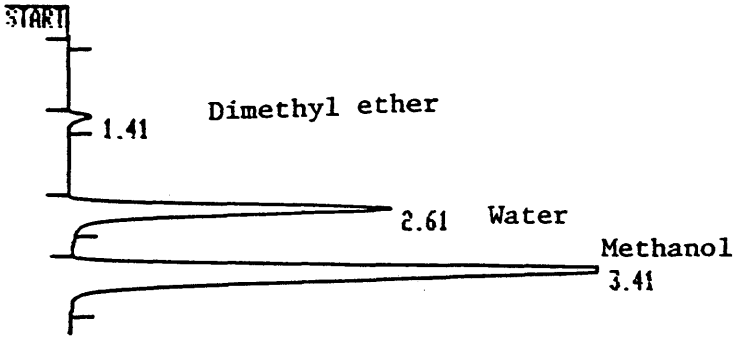
VARIAN 3700 GC Run Parameters

Anisole Reaction (Megabore Column)

Temperature (°C) / Isothermal)	60
Injector Temperature (°C)	280
Detector Temperature (°C)	250
Detector Current (mA)	273
Carrier Gas Flow Rate (cc/min.)	30

In each case the column is first conditioned and then followed by GC calibration of all components expected to show up in the products. Both columns have given very sharp and distinguished peaks. A chromatogram of the product mixture for both reactions, analyzed on the Varian-3700 GC is shown in Figures 7 and 8.

It was not possible to separate methanol, water and phenols with a single column. Porapak T, Q, and N, SP-1000, SP-2100, 15%SE30 packed columns were tested in the Varian GC. Commercial capillary and Megabore columns were also tested in the GC/MS. None of these were able to separate all components generated from the phenol alkylation with methanol. As a consequence, all results presented in the next section are given on a methanol and water-free basis.



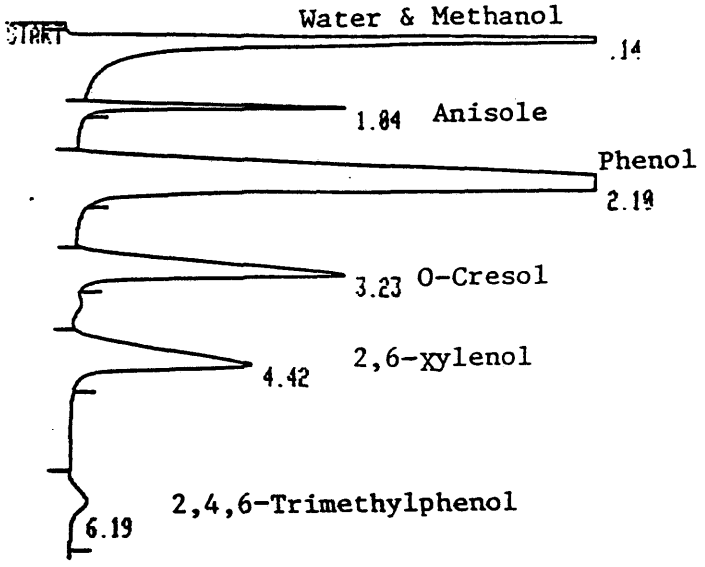
RUN # 14 JUL/04/89 19:00:41

AREA%

RT	AREA	TYPE	AR/HT	AREA%
1.41	6662	PB	0.090	1.083
2.61	171250	PB	0.156	27.827
3.41	437490	BB	0.210	71.091

TOTAL AREA= 615400
MUL FACTOR= 1.0000E+00

Figure 7. Sample Chromatogram from the Varian 3700 (Porapak T Column).



RUN # 2

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.14	239210	PB	0.034	43.858
1.04	14720	BB	0.066	2.699
2.10	196360	PB	0.286	36.002
3.23	48198	BB	0.210	8.837
4.42	41816	PB	0.271	7.667
6.19	5113	BB	0.323	0.937

TOTAL AREA= 545420
MUL FACTOR= 1.0000E+00

Figure 8. Sample Chromatogram from the Varian 3700 (Megabore Column).

V. RESULTS AND DISCUSSION

V.1. Experimental System Testing and Evaluation:

V.1.1. Preliminary System Shake-Down and Operation:

Preliminary system testing was carried out by flowing methanol through the system to check the pumping rate, pre-heater and heat-tracing functionality, operation of the reactor assembly, temperature and pressure control, and cooling system efficiency.

The Eldex pump used was found to require 5 psi pressure down stream to maintain operation. Multiple mass balance measurements were carried out at 350°C in the absence of any chemical reaction (no catalyst) and found to give essentially perfect closure (99.5% - 99.8%). The empty spinning-basket was also tested for alignment and found to have minimal vibration at 2000 RPM.

With the let-down needle valve originally installed (Autoclave Engineers, 10VRMM2812), the pressure in the reactor was very high (40 - 50 psi) and was found to fluctuate due to partial condensation in the valve. Heat-tracing of the product line upstream of the valve eliminated the pressure fluctuation, but the pressure drop across the let-down valve was still to high even at the full open position. For this reason, the let-down needle valve was replaced with a Whitey 316SS-21RS2 regulating valve. This valve typically comes with teflon packing which does not tolerate a temperature of more than 220°C, therefore the valve was repacked with graphite and put in service for testing. The new let-down valve was tested at 450°C and found to possess no leaks with pressure drop less than 2 psi at the maximum pumping rate (85 cc/hr) in the full open position.

The pre-heater was designed to deliver reactants to the reactor as a vapor (T_b of methanol=65°C, T_b of phenol=180°C). The pre-heater and the heating tape operation

was found to be adequate, with a 60% setting on the powerstat producing an outlet temperature of 240° C for an inlet temperature of 20° C. The furnace around the reactor was initially found to respond very slowly to changes in the set point and to generate a large overshoot (5 - 8 degrees). Therefore the temperature controller was tuned and set to a proportional gain, K_c of 1.0 and integral time constant T_I of 2.0 minutes. These values were found to give fast response and minimal temperature overshoot (1-2 degrees). This setting combination on the temperature controller was able to bring up the reactor temperature 50 degrees in about 40 minutes (72 - 76 degrees on the heater is equivalent to about 50 degrees on the reactor). These values will change slightly depending on heat of reaction and the flow rate to the reactor but are good enough to start up the system. The system was able to reach thermal steady state in about two hours.

The cooling system was designed to avoid any product losses. The system was originally designed with only one stage cooling (ice-bath cooling). However at a later point, it was decided to install an air cooling stage just after the let-down valve and before the ice-bath condenser. Operation of the system with methanol indicated that this combination gave less than 0.5% product losses under conditions of no reactions (no catalyst). The methanol outlet stream was analyzed to find out if the system material has any activity. The system material was found to be inert.

At this stage the reactor assembly was tested with catalyst in the spinning-basket at 2000 RPM. Distribution of equal amounts of catalyst in each side of the basket was very important to maintain balance and hence minimum vibrations. A difference of as little as 0.05 grams in the paddles of the spinning-basket resulted in excessive vibrations. The difference in catalyst loading was therefore always maintained at less than 0.04 gram.

V.1.2. Evaluation of Inter and Intra-Particle Mass Transfer Effects:

The operation of the CSTR was validated using methanol dehydration as the test reaction:

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$

The kinetics of this reaction have been determined by Cowley et al. , 1988. The catalyst tested was gamma alumina, and both alumina pellets and -20+30 mesh alumina particles were utilized in the CSTR. The main criteria considered for comparison was activation energy. The test was carried out at conditions similar to those of Cowley, that is 2 atmospheres total pressure, 200 - 300° C, and a WHSV of 5.12 g.feed/g.cat. hr..

The equation used in analysis of these data is the mass balance equation of a CSTR. This equation is as follows (assuming a perfectly mixed reactor):

$$r = (F_i - F_o)/ W.$$

where:

r : conversion rate of methanol to dimethyl ether and water (g.mol MeOH/hr.g.cat.).

F_i: molar feed rate of methanol (g.mol/hr).

F_o: molar rate of methanol in product (g.mol/hr).

W : Weight of catalyst (grams).

Because dimethyl ether (DME) could not be collected due to its high volatility, this product was accounted for by equating the amount DME to the amount of water produced. This assumption has been confirmed by Karpuk et al. for six types of catalysts and more than 70 data points at temperatures ranging from 200° to 350° C. Methanol dehydration reaction is a second order reaction. The rate equation reported by Karpuk et al. is as follows:

$$r = k C_m^2$$

r : conversion rate of methanol to DME and water (g.mol/hr g.cat).

C_m : methanol concentration (g.mol/cc).

k : second order rate constant (cc^2/g.mol hr g.cat).

The products of the methanol dehydration reaction were methanol, dimethyl ether, and water. The analysis was carried out in a Porapak T column packed at CSM by the author. Components were separated isothermally at 150° C. Diep et al., 1987, has carried out similar analysis for the same reaction in a Porapak Q packed column at 150° C. A sample chromatogram of the analysis was shown in the experimental section. Detailed rate calculations are given in Appendix 3 and Appendix 4.

Arrhenius plots of the rate constant for both catalysts pellets and the -20+30 mesh particles are shown in Figures 9 and 10. As can be seen, the plots are essentially perfectly linear ($R^2 \geq 0.995$) in all cases. This observation combined with the experimental value for E_a (apparent activation energy) indicates that activation energy is for chemical reaction, does not vary with temperature, and hence confirms the absence of any internal diffusion (pore diffusional mass transfer) as the rate limiting step.

The activation energy for methanol dehydration obtained by Karpuk et al., in his tubular flow reactor system was 23.00 Kcal/mol. The activation energy obtained in the CSTR designed in this research was found to be 23.56 Kcal/mol. This finding also indicates the absence of any external mass transfer influence on the chemical reaction rate.

The effectiveness factor, η, for the methanol dehydration test reaction was determined experimentally. Effectiveness factor, η, is defined as follows :

$$\eta = \frac{\text{rate of the pellet}}{\text{rate of the particles}}$$

The effectiveness factor was calculated for both the γ-alumina pellets and -20+30 mesh

particles. The mean effectiveness factor for six different rate points was found to be 1.00. This is another major criteria that confirms the operation of the CSTR. Negligible pore diffusion in the case of the γ-alumina catalyst has been also reported by Ionescu, 1986 in the anisole reaction study.

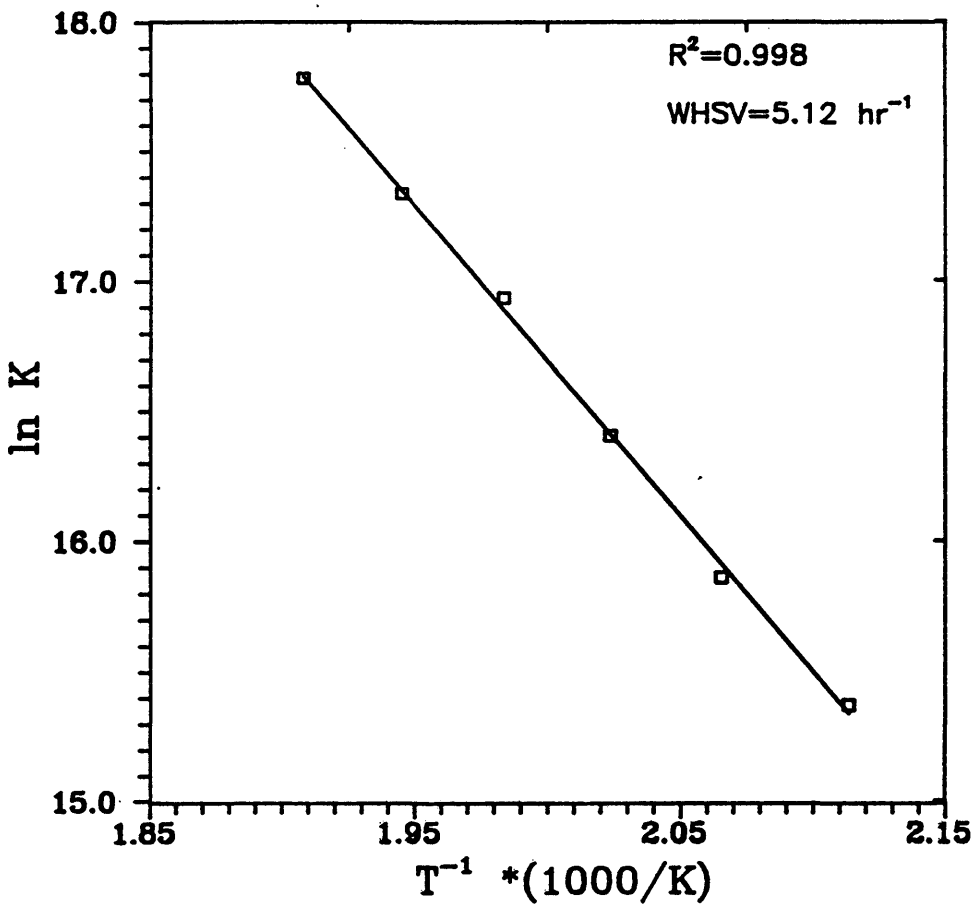


Figure 9. Arrhenius Plot for Methanol Dehydration on γ-Alumina Catalyst Pellet.

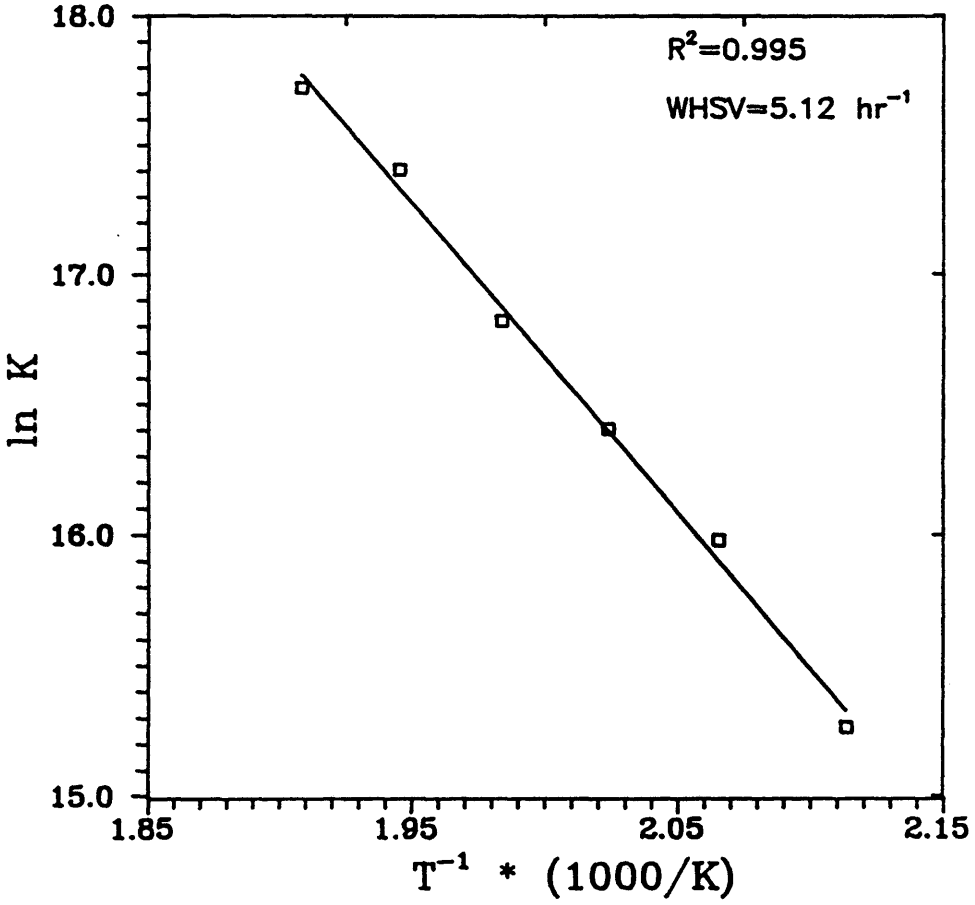


Figure 10. Arrhenius Plot for Methanol Dehydration on -20+30 γ-Alumina Particles.

V.1.3 Evaluation of External Mass Transfer:

The effect of inter-particle mass transfer on the rate of methanol dehydration was evaluated at a temperature of 350° C where the rate of chemical reaction is rapid and transport process are more likely to be rate limiting. The test was carried out by measuring the rate at different stirring speeds. Steady state was established and confirmed by considering the reproducibility of analyses among multiple measurements. The results of this test are shown in Figure 11. Detailed calculations are given in Appendix 5. The minimum stirring speed was found to be 1510 RPM. Below 1510 RPM, the rate start dropping thus indicating the onset of external diffusional resistances.

Carberry, 1964, has found the minimum speed to eliminate external mass transfer to be 1600 RPM at temperature range of 200 - 234° C for the CO oxidation reaction. Tajbl, 1969, determined the minimum RPM speed in his CSTR and found it to be 2000 RPM at 200 - 250° C for hydrogenolysis of ethane and propane.

The catalytic CSTR designed in this research has thus shown excellent operation in terms of elimination of transport processes. The size of the catalyst basket played a significant role in providing a high catalyst loading capacity. The clearance between the basket and the reactor wall is 0.08 inch. The shoulders designed in the shaft provided a balanced seating for the basket which led to perfect alignment. Therefore, oscillation was eliminated completely at high RPM's and problems associated with bearing failure that normally plague these types of reactors were not experienced during this project. The reactor was operated for a period of time in excess of 500 hours and no bearing failures were ever experienced.

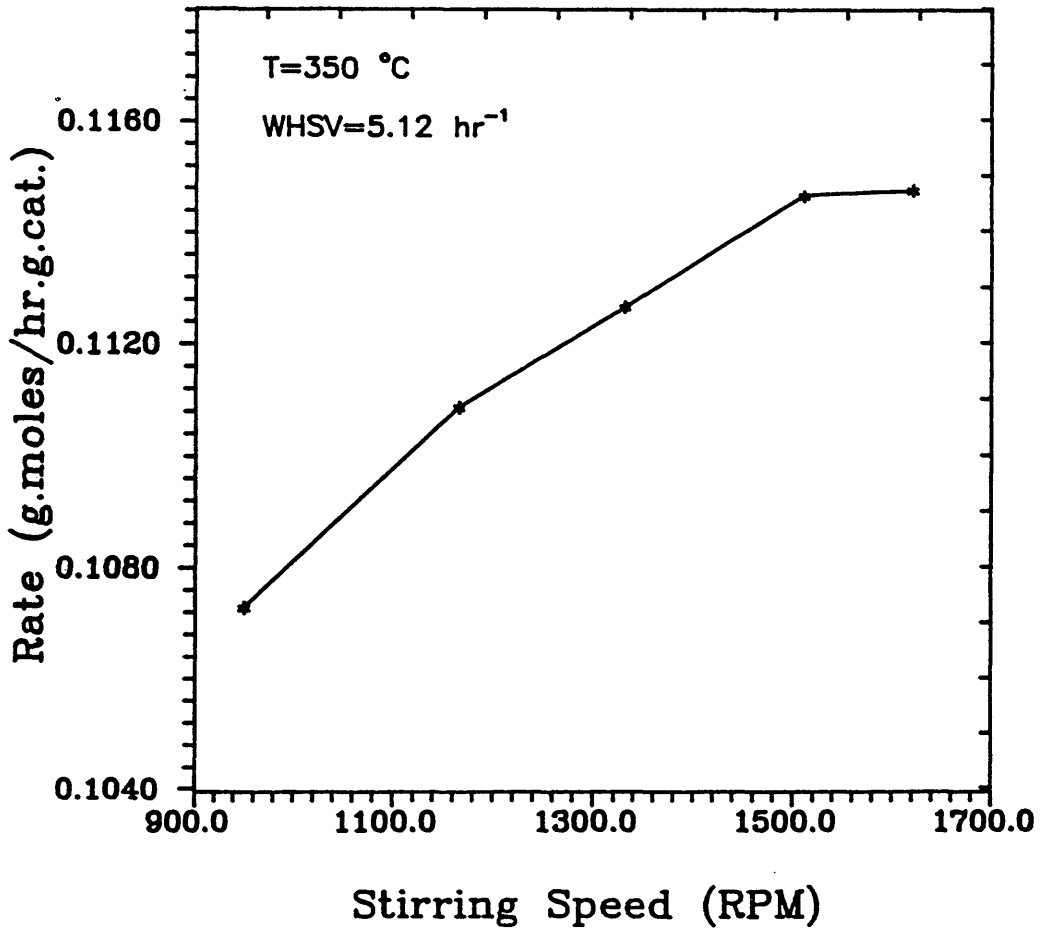


Figure 11. Rate versus Stirring Speed.

V.2. Synthesis of Anisole :

As mentioned earlier in this thesis, the reaction of methanol and phenol is highly coupled due to two simultaneous reactions that can take place. The most recent reaction mechanism has been reported by Ionescu, 1986, (shown previously in the literature survey) indicates that both anisole and o-cresol can be formed by alkylation of phenol with methanol.

Operating conditions where anisole was a by-product of the alkylation of phenol with methanol have been reported by Nozaki and Ionescu as follows:

WHSV	$\geq 5.0\ hr^{-1}$
Temperature	$> 250^{\circ} C$
Pressure	= 1 atm.
Feed molar ratio	= 1:2 phenol : methanol
Catalyst	γ Alumina, $Ca_3(PO_4)$, $CaHPO_4$, $Ca(H_2PO_4)_2$, BPO_4, CaO and MgO.

On this basis, it was decided to carry out the preliminary investigations on anisole production at the following operating conditions:

WHSV	$\leq 5.0\ hr^{-1}$
Temperature	= 250-350° C
Pressure	= 1 atm.
Feed molar ratio	= 1:2 phenol : methanol

The following sections present detailed results and discussion of all catalysts evaluated for this reaction.

V.2.1. γ-Alumina Catalysts:

The first catalyst tested were unmodified γ-alumina. Both catalyst pellets and -20+30 mesh particles were employed for this portion of study. The results for each catalyst in terms of activity and selectivity on a molar basis are given in Tables 5 and 6. These results are presented as product compositions on a water and methanol-free basis. As mentioned previously, no analytical system capable of separating methanol and water in the presence of phenols was developed during the course of this research. As a result, the exact composition of the products could not be determined and catalyst activity and selectivity were computed by the following expression (methanol and water-free basis):

$$\text{Activity} = 100 - \text{mole \% of phenol in products}$$

$$\text{Selectivity} = \text{mole \% of anisole in products / Activity}$$

Three dimensional bar charts of activity and selectivity are presented in Figures 12, 13.

As can be seen from these results, the γ-alumina catalyst favored the methyl alkylation of phenol to cresols as temperature increased. The concentration of o-cresol in the products at 300°C is five times that found at 250°C. This increase in methyl alkylated products caused a major drop in selectivity toward formation of anisole. At 350°C, further methyl alkylation started taking place and higher alkylated products such 2,6-xylenol and 2,4,6-trimethylphenol started showing up with no further drop in anisole selectivity. These observations agreed qualitatively with the observations of Ionescu and Nozaki. A direct comparison however is not possible due to the fact that the work of Ionescu and Nozaki work was carried out in tubular flow reactors.

The thermodynamic calculations shown in Appendix 5 and summarized in Tables 7 and 8 confirm the experimental observations mentioned above. The thermodynamic cal-

culations were carried out using the group contribution methods of Van Krevelen, 1951, to determine the free energy of formation of anisole. As can be seen, the reaction pathway for the formation of o-cresol at temperatures in the range of 300 K - 800 K has a lower free energy and hence is more favored than that for anisole. The mechanism proposed by Ionescu also indicated this fact, where the reaction pathway for formation of o-cresol was represented as irreversible and reversible in the case of anisole .

Table 5

Product Composition (mole%) for γ-alumina catalyst pellet[1,2]

	Mole %		
Component	250°C	300°C	350°C
Anisole	11.01	5.26	3.20
O-Cresol	7.58	15.56	17.31
2,6-Xylenol	2.18	10.50	8.88
2,4,6-Trimethylphenol	0.0	1.95	2.63
Phenol	79.23	66.72	67.99
Activity	20.77	33.28	32.01
Selectivity	53.00	15.82	9.99

1 : WHSV=5.0 hr^{-1}

2 : Compositions reported on methanol and water-free basis

Table 6

Product Composition (mole%) for γ-alumina catalyst (-20+30 mesh particles)[1,2]

	Mole %		
Component	250°C	300°C	350°C
Anisole	11.94	4.14	3.24
O-Cresol	9.36	15.91	18.21
2,6-Xylenol	3.23	11.26	7.34
2,4,6-Trimethylphenol	0.0	2.69	2.74
Phenol	75.47	66.00	68.48
Activity	24.53	34.00	31.52
Selectivity	48.66	12.18	10.27

1 : WHSV=5.0 hr^{-1}

2 : Compositions reported on methanol and water-free basis

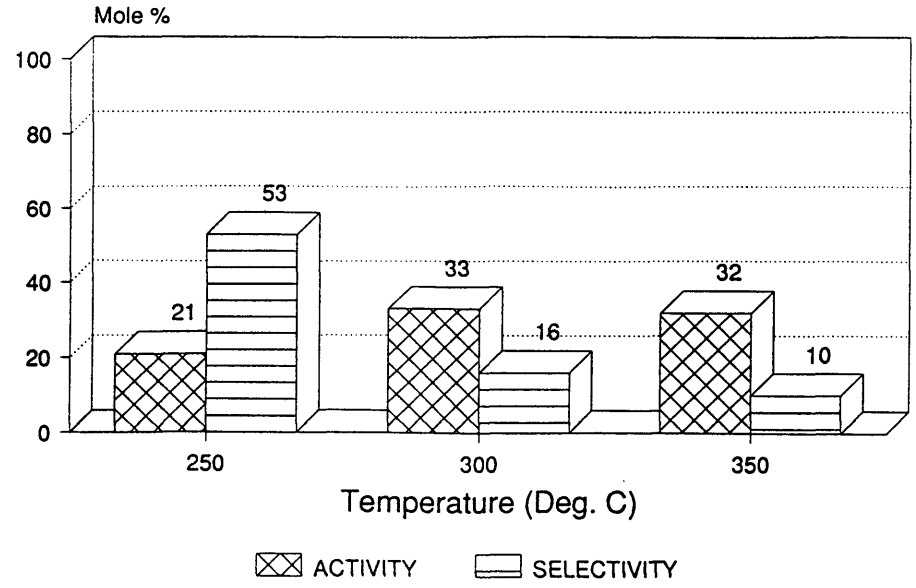


Figure 12. Activity and selectivity of γ-Alumina Catalyst Pellet (WHSV=5.0 hr^{-1}).

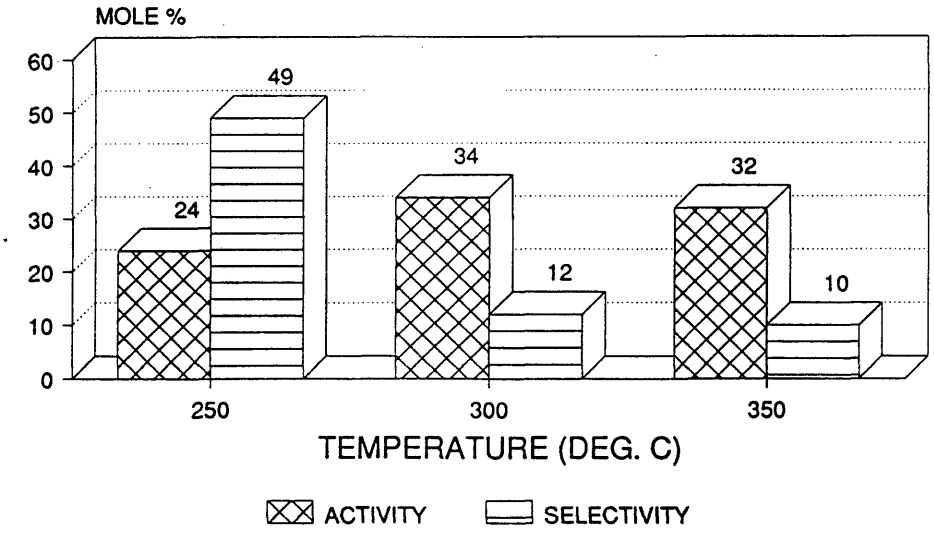
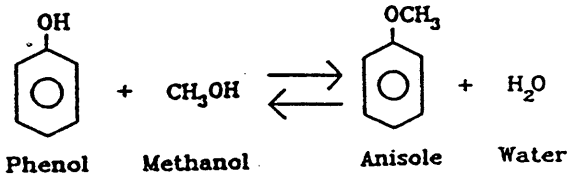


Figure 13. Activity and selectivity of -20+30 γ-Alumina Catalyst Particles (WHSV=5.0 hr^{-1}).

Table 7

Equilibrium Calculations Based on Van Krevelen

$$\Delta G_{rxn} = \Delta G_{products} - \Delta G_{reactants}$$

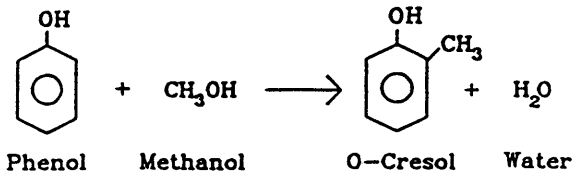


Temperature(K)	ΔG_{rxn} (Kcal/mole)	$K_{equilibrium}$
300	2.945	0.0072
400	1.48	0.1553
500	-0.243	1.277
600	-2.41	7.550

Table 8

Equilibrium Calculations Based Tabulated Data

$$\Delta G_{rxn} = \Delta G_{products} - \Delta G_{reactants}$$



Temperature(K)	ΔG_{rxn} (Kcal/mole)	$K_{equilibrium}$
300	-16.79	$1.71*10^{12}$
400	-16.64	$1.24*10^{09}$
500	-16.55	$1.72*10^{07}$
600	-16.54	$1.06*10^{06}$
800	-16.56	$3.34*10^{04}$

V.2.2. Proposed Surface Mechanism:

A proposed mechanism for anisole formation is presented in Figure 14. Structure I illustrates the possible reasonance forms present on a hydrated γ-alumina catalyst surface. Methanol is first associatively adsorbed on the surface forming an adsorbed methanol and followed dissociatively adsorption forming an adsorbed methoxy group and hydroxy group as shown in structure's II and III. Dissociative adsorption of phenol occurs in a similar manner as shown in IV. The methyl group is transferred to the phenoxy oxygen via a nucleophilic displacement mechanism to form an associatively adsorbed anisole species. Desorption of anisole and water regenerate the catalyst surface.

A proposed mechanism for o-cresol formation over γ-alumina catalyst is also presented in Figure 15. Structure I shows the dissociative adsorption of phenol and methanol. Electrophilic attack of a surface methyl carbocation on the aromatic ring produces a sigma complex shown in structure III. A surface oxygen anion removes a proton from the sigma complex to form the dissociatively o-cresol species, thus the subsequent desorption of o-cresol regenerates the surface.

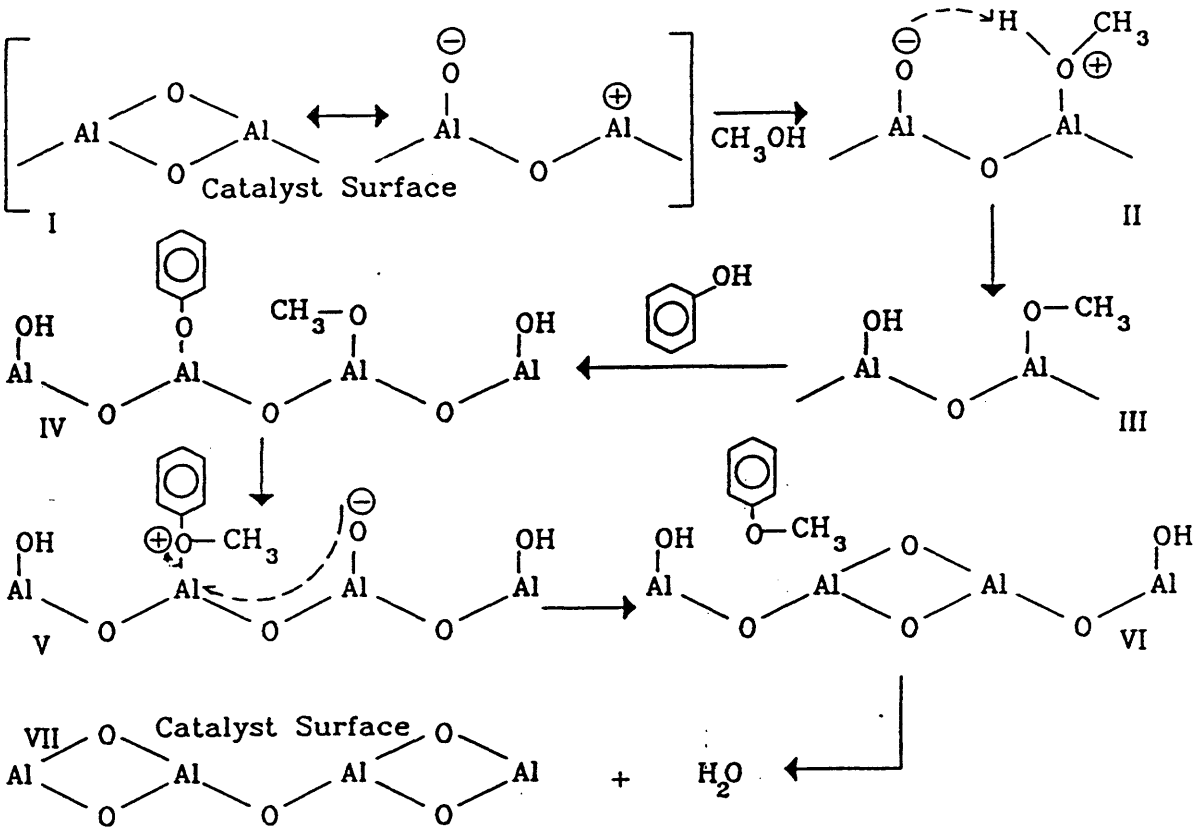


Figure 14. Proposed Surface Mechanism for Anisole Formation over Lewis-Acid Catalyst (γ-Alumina).

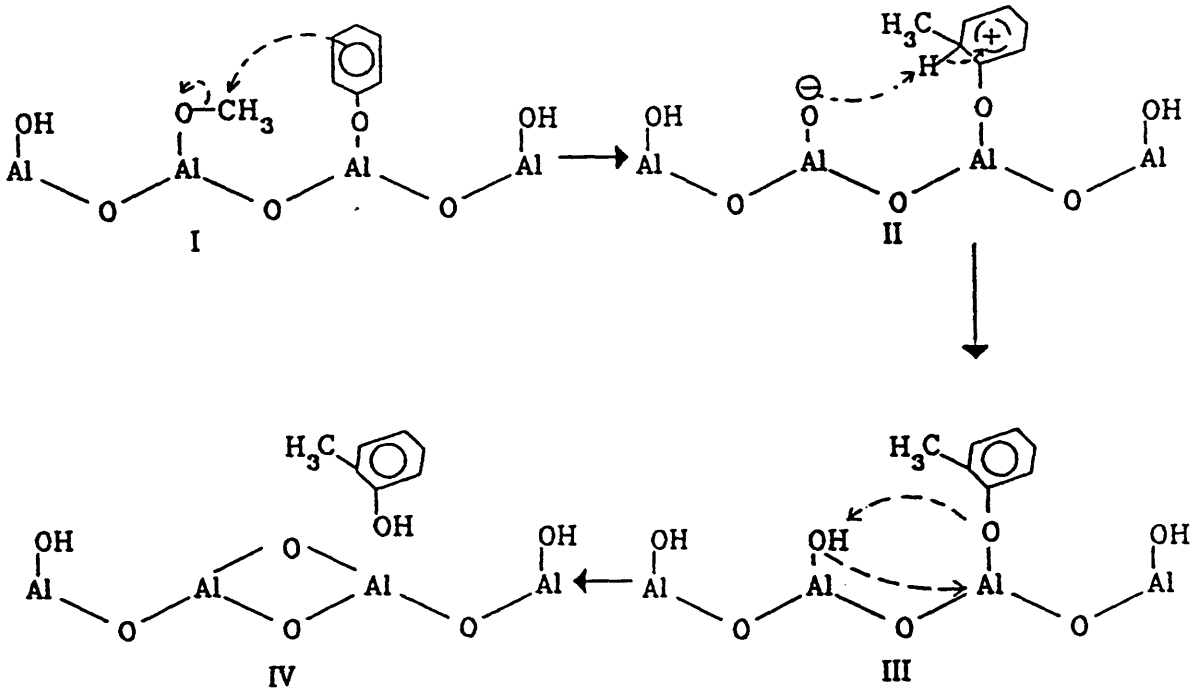


Figure 15. Proposed Surface Mechanism for O-cresol Formation over Lewis-Acid Catalyst (γ-Alumina).

V.2.3. Phosphated γ-Alumina catalysts

Phosphated γ-alumina catalysts of 0.5 and 0.8 phosphorus-to-alumina atomic ratio were prepared by a co-precipitation technique, and their activity and selectivity for anisole production evaluated. Results in terms of product compositions on a water and methanol-free basis are presented in Tables 9 and 10. Activity and selectivity are shown graphically in Figures 16 and 17.

The presence of phosphate on the catalyst eliminated the formation of trialkylated products, i.e 2,4,6-trimethylphenol. This observation also was seen by Maholland (1987) and Erickson (1989), and can possibly be attributed to the increase in acidity caused by the presence of phosphorus (Maholland, 1987).

The product distribution for the 0.5 P/Al catalyst particles in the temperature range from 250 to 350° C is shown in Table 9. As can be seen, the activity of this catalyst remained essentially constant as temperature changed while the selectivity at 350° C dropped to about 42% the selectivity found at 250° C. This drop in selectivity for formation of anisole was accompanied by an increase in the formation of the mono-alkylated product (o-cresol). Results for the 0.8% P/Al catalyst shown in Table 10 indicate a small drop in activity as temperature is increased from 250 to 350° C, and a very substantial drop in selectivity. For the 0.8 P/Al catalyst, the selectivity at 350° C is only about half (53% decrease) the selectivity found at 250° C. As was the case for the 0.5 P/Al catalyst, this drop in selectivity was accompanied by an increase in production of o-cresol although this increase was less than that found for the 0.5 P/Al catalyst. Apparently the increase in the phosphate content decreased the rate of formation of o-cresol and increased the rate of formation of anisole. This subsequently resulted in less reduction of

selectivity in the case of 0.8 P/Al catalyst as temperature increased.

At 350°C, the amount of 2,6-xylenol in the product from both 0.5 and 0.8 P/Al catalysts dropped to approximately one half the amount produced by the unmodified γ-alumina catalysts. Formation of o-cresol dropped significantly at 350°C for the 0.8 P/Al catalyst, but remain unchanged for the 0.5 P/Al catalyst.

The Brönsted-acid catalyst (phosphated alumina) was found to be more selective than The Lewis-acid catalyst (γ-alumina). This could be due to the acidity of the surface where the phenols are adsorbed in a flat position, parallel to the surface, while on a non-acidic surface the phenolate form interacted, via oxygen, perpendicular to the surface. Due to the high surface acidity, the acid sites interact with the pi-electron giving the flat adsorption form. Such an interaction is not feasible on a weakly acidic surface and the perpendicular form predominates (Maholland, 1987).

Table 9

Product Composition (mole%) for 0.5 P/Al catalyst(-14+20 mesh)[1,2]

	Mole %		
Component	250°C	300°C	350°C
Anisole	18.20	12.40	7.80
O-Cresol	9.10	14.20	18.10
2,6-Xylenol	3.40	5.80	4.80
2,4,6-Trimethylphenol	0.00	0.00	0.00
Phenol	69.30	67.60	69.30
Activity	30.70	32.40	30.70
Selectivity	59.28	38.27	25.41

1 : WHSV=5.0 hr^{-1}

2 : Compositions reported on methanol and water-free basis

Table 10

Product Composition (mole%) for 0.8 P/Al catalyst(-14+20 mesh)[1,2]

	Mole %		
Component	250°C	300°C	350°C
Anisole	18.60	13.90	9.20
O-Cresol	8.60	12.60	14.80
2,6-Xylenol	2.90	4.40	4.20
2,4,6-Trimethylphenol	0.00	0.00	0.00
Phenol	69.90	69.00	71.70
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Activity	30.10	31.00	28.30
Selectivity	61.79	44.84	32.51

1 : WHSV=5.0 hr^{-1}

2 : Compositions reported on methanol and water-free basis

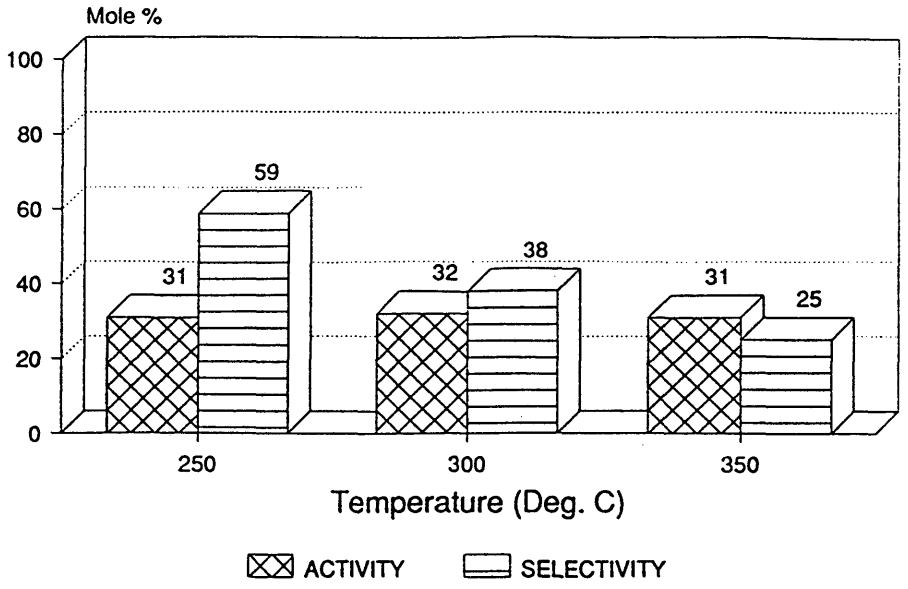

Figure 16. Activity and Selectivity for 0.5 P/Al Catalyst.

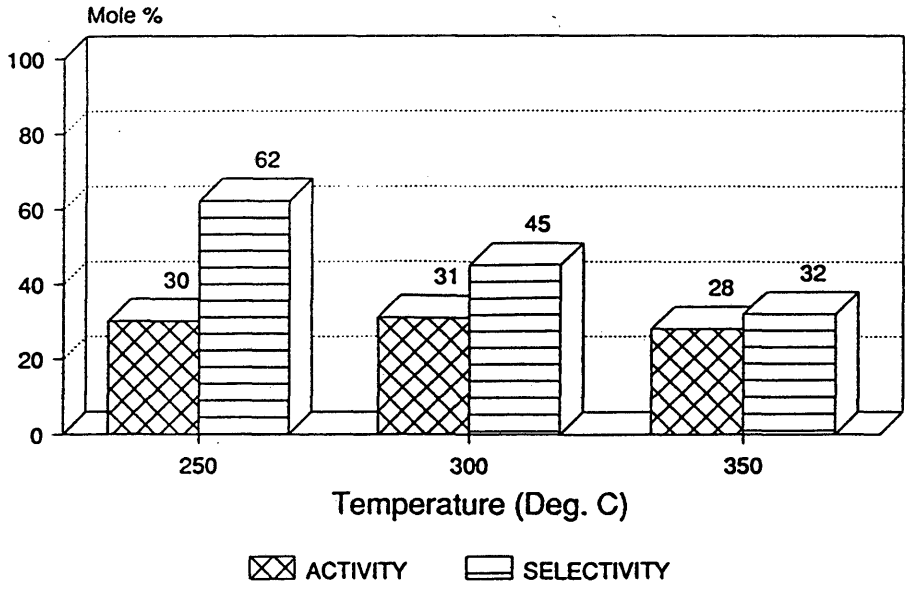

Figure 17. Activity and Selectivity for 0.8 P/Al Catalyst.

V.2.4. Proposed Surface Mechanism:

A proposed surface mechanism for the formation of anisole over the phosphated γ-alumina catalyst is presented in Figure 18. Methanol is dissociatively adsorbed on the surface forming adsorbed water and a methyl carbocation which is associated with the phosphate group. The methyl carbocation can react with a phenol molecule in the vapor space, a Rideal type mechanism, or it can react with a phenol molecule which is dissociatvely adsorbed on an adjacent alumina Lewis acid site. The anisole produced is then desorbed from the surface. An analogous mechanism for the o-cresol formation is presented in Figure 19. In this case the carbocation reacts with the aromatic ring rather than the oxygen atom to form the alkylated product.

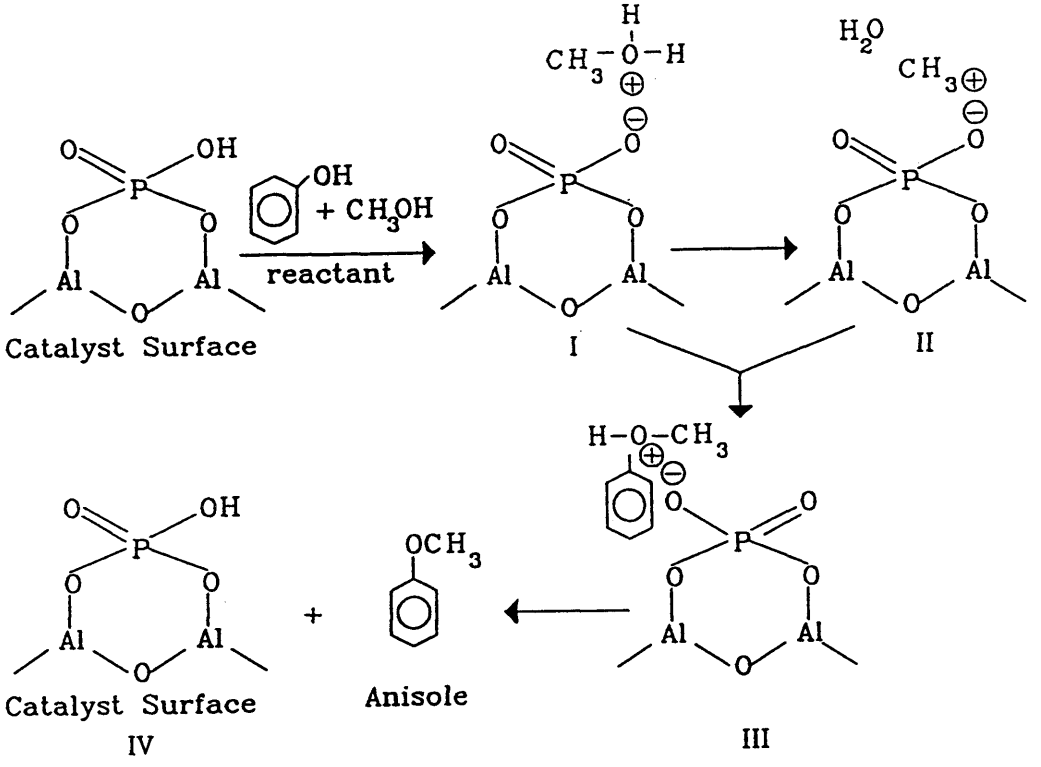

Figure 18. Proposed Surface Mechanism for Anisole Formation over Brönsted-Acid Catalyst (0.5 P/Al).

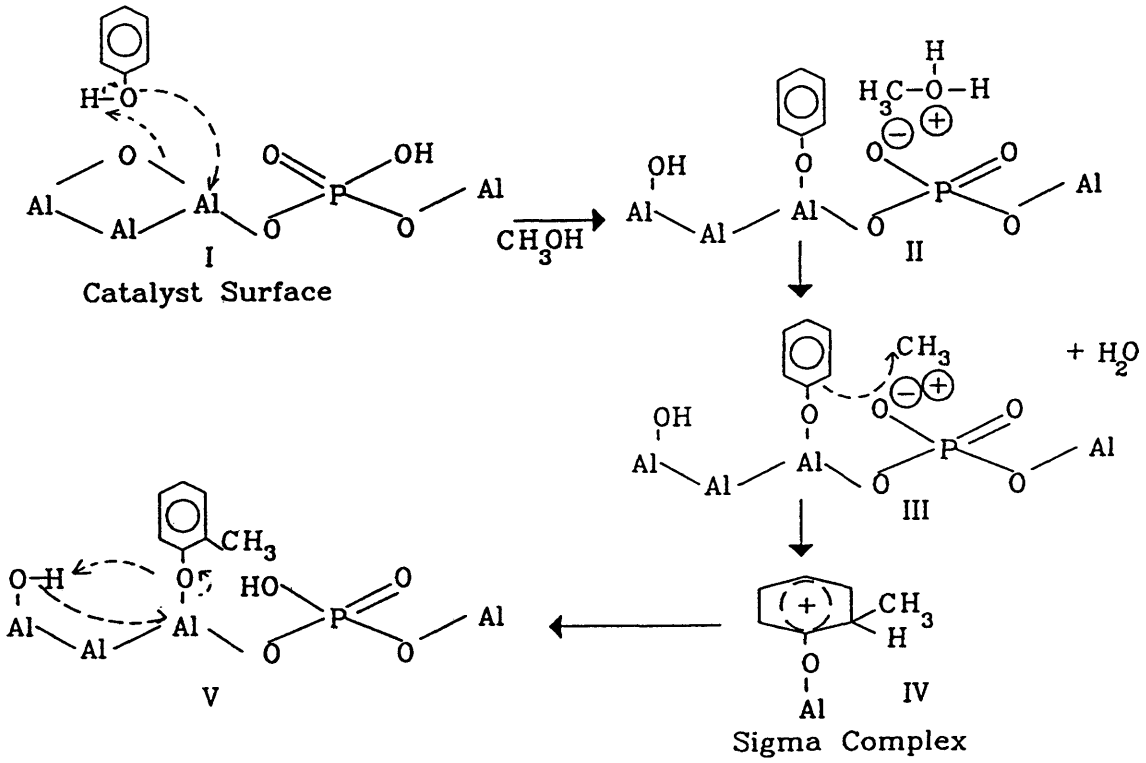

Figure 19. Proposed Surface Mechanism for O-Cresol Formation over Brönsted-Acid Catalyst (0.8 P/Al).

V.2.5. The Base Catalysts

The Lewis and Brönsted acid catalysts examined up to this point have exhibited fairly high activity but low selectivity over the range of temperature and space velocities tested. The reasons for experimenting with a base catalyst at this point are as follows:

1. The acid catalysts tested so far exhibited poor selectivity with respect to formation of anisole.
2. Base catalysts can catalyze formation of anisole via a different mechanism which eliminates the possibility of alkylation of aromatic rings. Figure 20 is a proposed mechanism for anisole formation on a base catalyst.

As a test of this hypothesis, a 10% solution of Na_2HPO_4 was impregnated on a silica support and tested at the same conditions utilized for the acid catalysts. Results in terms of product compositions on a water and methanol-free basis are presented in Table 11. Activity and selectivity are shown in Figure 21. The methyl alkylation reaction was shut down completely at 250° C and 300° C, giving 100% selectivity. Activity was still fairly low relative to the acid catalysts. At 350° C, the activity has increased about 3 times the activity at 300° C but the drop in selectivity was only 6%. The higher alkylated products such as 2,6-Xylenol and 2,4,6-trimethylphenol did not show up at all.

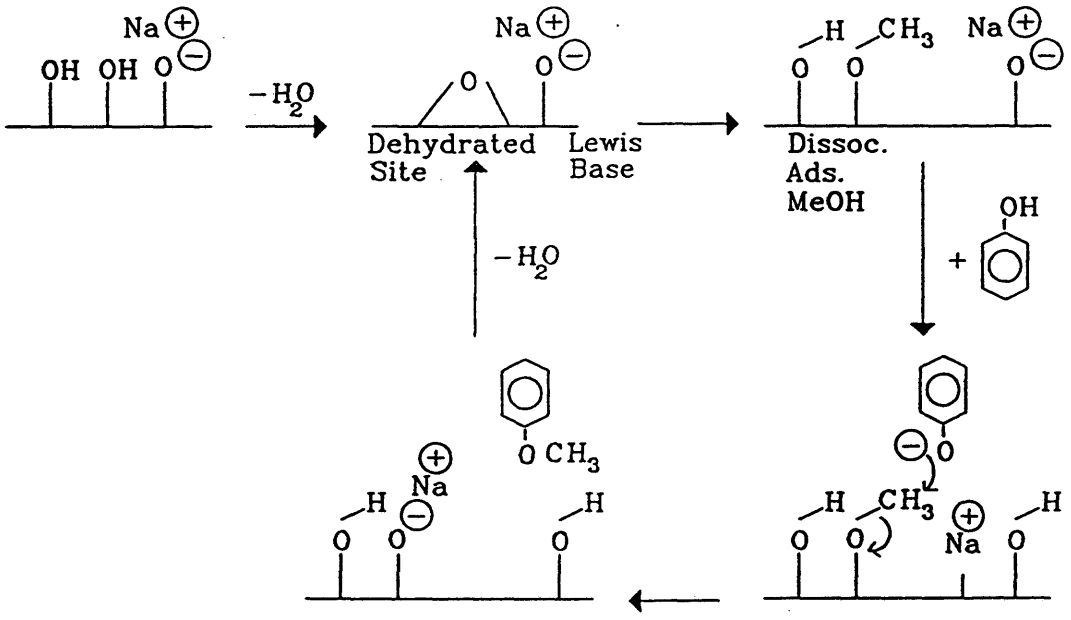

Figure 20. Proposed Surface Mechanism for Anisole Formation over a Base Catalyst.

Table 11

Product Composition (mole%) for 10% Na_2HPO_4 catalyst(-14+20 mesh)[1,2]

	Mole %		
Component	250°C	300°C	350°C
Anisole	0.30	1.67	4.69
O-Cresol	0.00	0.00	0.35
2,6-Xylenol	0.00	0.00	0.00
2,4,6-Trimethylphenol	0.00	0.00	0.00
Phenol	99.70	98.32	95.01
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Activity	0.3	2.00	5.0
Selectivity	100.00	100.00	94.00

1 : WHSV=5.0 hr^{-1}

2 : Compositions reported on methanol and water-free basis

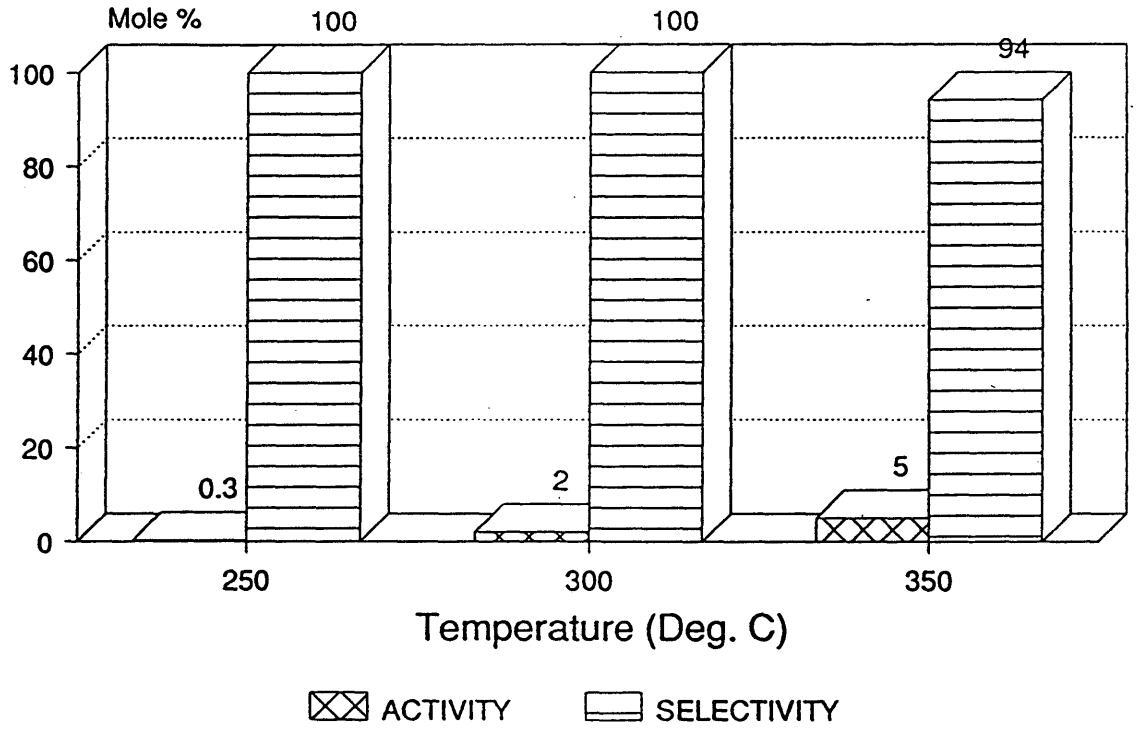

Figure 21. Activity and Selectivity for 10% Na_2HPO_4 Catalyst.

These results looked very promising. Further testing was considered particularly at lower space velocities and higher temperatures in order to achieve higher conversions and hence an improved yield for anisole. The sodium base catalyst tested originally was also tested at 400° C and found to start deactivating (catalyst stability testing is described in the next section). Thus 350° C was found to be the maximum stable temperature where the catalyst did not undergo significant deactivation. The same base catalyst (same batch) was subsequently tested at the lowest possible space velocity that would be provided by the existing pump. At 350° C and a WHSV of 1.5 g.feed/g.cat. hr., the activity was found to be almost double the activity found at a WHSV of 5.0 g.feed/g.cat. hr. The selectivity dropped to 88%, and again the higher alkylated products (2,6-xylenol and 2,4,6-trimethyl-phenol) were not produced. These results are shown in Table 12. The activity and selectivity are presented graphically in Figure 22.

At this point before proceeding further, the silica support was tested at high temperature and the lowest space velocity and found to posses no activity. This confirmed that the activity was provided only by the catalytic material impregnated on the support.

A batch of catalyst was prepared by impregnation of a silica support from 20% solution of Na_2HPO_4) following exactly the same preparation procedure as in the case of 10% loading. This material was tested at 350° C and the same velocities as those tested previously with the 10% catalyst. The activity and selectivity were found essentially the same. These results are shown in Table 13, while activity and selectivity are shown in Figure 23.

Table 12

Product Composition (mole%) for 10% Na_2HPO_4 catalyst(-14+20 mesh)[1,2]

	hr^{-1}		
Component	1.50	3.64	7.30*
Anisole	10.45	5.84	2.32
O-Cresol	1.22	0.50	0.00
2,6-Xylenol	0.00	0.00	0.00
2,4,6-Trimethylphenol	0.00	0.00	0.00
Phenol	88.33	93.66	97.68
---	---	---	---
Activity	11.67	6.34	2.32
Selectivity	89.54	92.11	100.00

1 : Temperature = 350°C

2 : compositions reported on methanol and water-free basis

Table 13

Product Composition (mole%) for 20% Na_2HPO_4 catalyst(-14+20 mesh)[1,2]

	hr^{-1}		
Component	1.70	3.30	6.94*
Anisole	11.32	8.24	5.36
O-Cresol	1.32	0.61	0.31
2,6-Xylenol	0.00	0.00	0.00
2,4,6-Trimethylphenol	0.00	0.00	0.00
Phenol	87.36	91.14	94.33
Activity	12.64	8.86	5.67
Selectivity	89.56	93.00	94.53

1 : Temperature = 350°C

2 : compositions reported on methanol and water-free basis

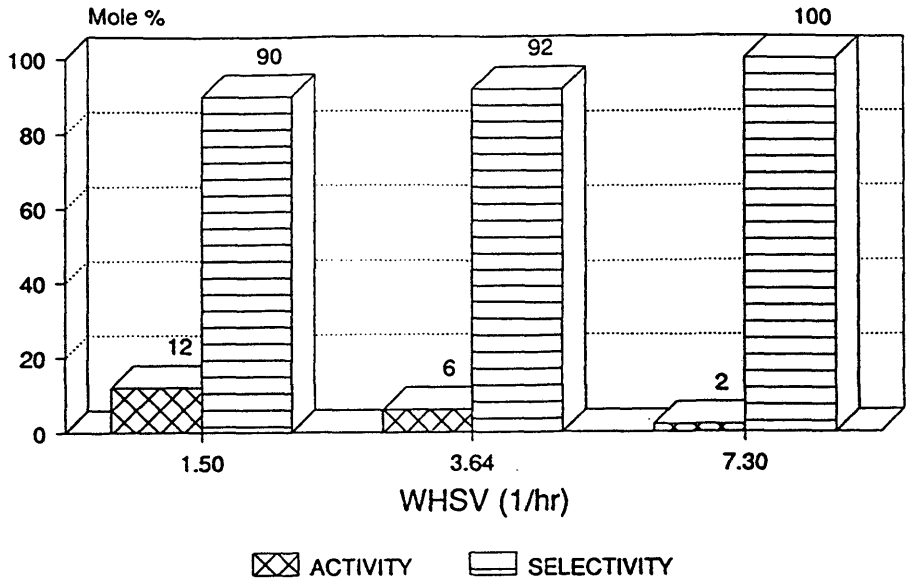

Figure 22. Activity and Selectivity for 10% Na_2HPO_4 Catalyst.

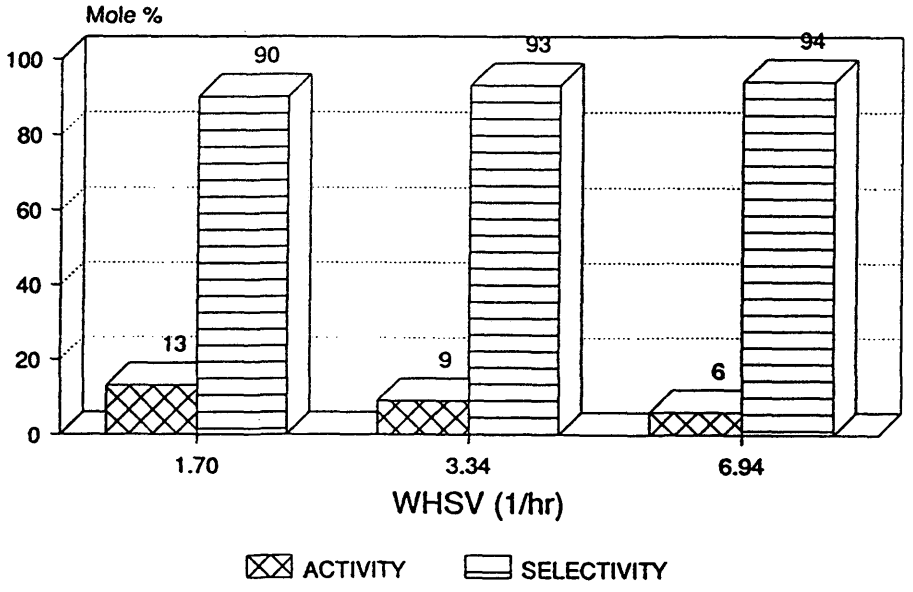

Figure 23. Activity and Selectivity for 20% Na_2HPO_4 Catalyst.

V.3 Stability Tests:

All base catalysts evaluated in this thesis for the production of anisole were tested for stability with respect to retention of activity. This test was carried out by taking data at a series of temperature levels between 250 and 400 °C in increments of 50° C. The system was allowed to stabilize and attain steady state at each temperature level and products were collected over a period of approximately 2 hours, after which time the system was returned to 250° C and catalyst activity measured. Schematically, this routine appears as follows:

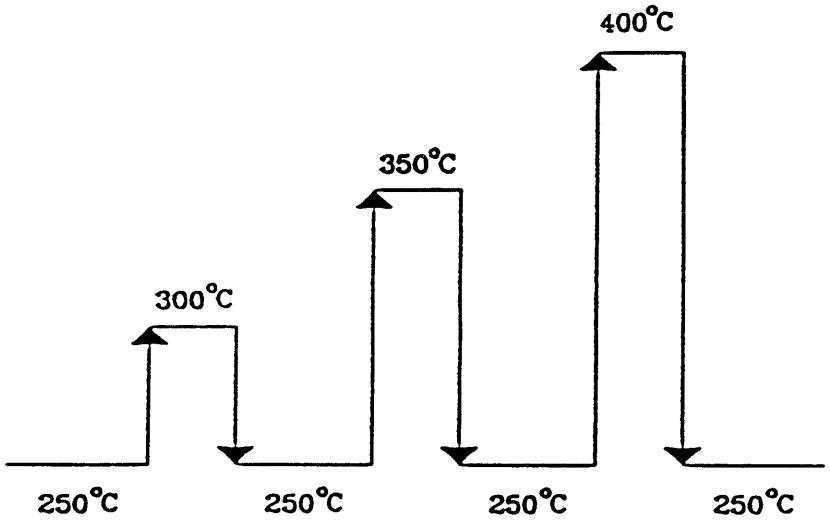

Figure 24. Temperature Pathway for the Stability Test

Results of this test indicated that the catalyst activity at 250° C was not changed following operation at 300 and 350° C, but was substantially lowered (52%) after operation at 400° C. This observation confirmed that catalyst deactivation had taken place at the higher temperature. The catalyst appeared to be black upon completion of this run sequence, suggesting that coking of the reactants had taken place on the catalyst surface.

VI. CONCLUSIONS

VI.1. The CSTR System:

The spinning-basket catalyst testing system designed and utilized for this study has given satisfactory operation.

VI.2. Anisole Synthesis:

The Lewis-acid catalyst (γ-alumina) was found to be less selective than the Brönsted-acid catalyst (phosphated alumina).

At a temperature of 350°C the selectivity of the Brönsted-acid catalyst was three times that of the Lewis-acid catalyst. The difference in activity between these two catalysts was, however, negligible.

The base catalyst was found to be a better catalyst in terms of selectivity for formation of anisole. The activity of the base catalyst was, however, somewhat lower (about half) than the activity of either of the acid catalysts at the lowest space velocity tested (1.5 g.feed/g.cat.hr).

VII. RECOMMENDATIONS

1. Base catalysts should be investigated in more detail. Efforts should focus on improvement of activity since thermodynamic calculations indicate that equilibrium has not yet been achieved at the temperatures studied.
2. The production of anisole can be carried out in a tubular flow reactor where back mixing is eliminated hence giving a better indication of catalyst activity.
3. Complete analysis of products should be investigated further.
4. Kinetics of the reaction over base catalysts should be investigated.

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APPENDIX 1

GC Calibrations

TABLE (14)

GC Calibration

Methanol Dehydration Reaction

Porapak T Column

5 WT.% H_2O

COMP.	DENSITY gm/cc	WT.FRAC.	MEAN GC AREA	C.F WT.	CF MOL.
H_2O	1.00	0.05	28512	**0.771**	**1.37**
MeOH	0.7931	0.95	417550	**1.00**	**1.00**

10 WT.% H_2O

COMP.	DENSITY gm/cc	WT.FRAC.	MEAN GC AREA	C.F WT.	CF MOL.
H_2O	1.00	0.10	66985	**0.794**	**1.41**
MeOH	0.7931	0.90	479030	**1.00**	**1.00**

20 WT.% H_2O

COMP.	DENSITY gm/cc	WT.FRAC.	MEAN GC AREA	C.F WT.	CF MOL.
H_2O	1.00	0.20	132820	**0.773**	**1.37**
MeOH	0.7931	0.80	410810	**1.00**	**1.00**

35 WT.% H_2O

COMP.	DENSITY gm/cc	WT.FRAC.	MEAN GC AREA	C.F WT.	CF MOL.
H_2O	1.00	0.35	162740	**0.800**	**1.43**
MeOH	0.7931	0.65	242537	**1.00**	**1.00**

50 WT.% H_2O

COMP.	DENSITY gm/cc	WT.FRAC.	MEAN GC AREA	C.F WT.	CF MOL.
H_2O	1.00	0.50	246200	**0.793**	**1.41**
MeOH	0.7931	0.50	199955	**1.00**	**1.00**

TABLE (15)

GC Calibration

Anisole Reaction

Megabore Column

Comp.	DENSITY gm/cc	WT. FRAC.	MEAN GC AREA	C.F Wt.
Anisole	0.994	0.178	26576	**1.000**
Phenol	1.132	0.230	35623	**1.037**
O-cresol	1.0273	0.330	49878	**1.012**
2,6-Xylenol	0.928	0.126	20748	**1.102**
2,4,6-Tri-methylphenol.	l0.8798	0.136	21414	**1.055**

APPENDIX 2

Rate Calculations for the γ-Alumina Pellets and Particles catalysts

CATALYST	:	Pellet, γ-alumina
rpm	:	1600
Temp.	:	200 °C
Mass of cat.	:	9.6887 gram
Actual mass in	:	51.948g/hr , feed.
Actual mass out	:	48.63 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	2553	1.7	4340.1	0.952
H_2O	8639	0.8	6911.2	1.515
MeOH	444860	1.0	444860	97.533

Mass out(MeOH+H_2O)=48.167 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	8639	1.4	12094.6	2.647
MeOH	444860	1.0	444860	97.353

AVG. MWt.	31.629 g/g.mole
Moles MeOH out	1.4826 g.mole/hr
Moles MeOH in	1.6234 g.mole/hr
Conversion, X	8.6746%
Rate	0.0145 g.moles/hr.g.cat.

CATALYST	:	Pellet,γ-alumina
rpm	:	1600
Temp.	:	212 °C
Mass of cat.	:	9.6887 gram
Actual mass in	:	51.948 g/hr , feed.
Actual mass out	:	47.4 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	5169	1.7	8787.3	1.774
H_2O	14005	0.8	11204	2.261
MeOH	475440	1.0	475440	95.965

Mass out(MeOH+H_2O)=46.559 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	14005	1.4	19607	3.961
MeOH	475440	1.0	475440	96.039

AVG. MWt.	31.446 g/g.mole
Moles MeOH out	1.422 g.mole/hr
Moles MeOH in	1.6234 g.mole/hr
Conversion, X	12.405%
Rate	0.0208 g.moles/hr.g.cat.

CATALYST	:	Pellet,γ-alumina
rpm	:	1600
Temp.	:	221°C
Mass of cat.	:	9.6887 gram
Actual mass in	:	51.948g/hr , feed.
Actual mass out	:	46.2 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	8346	1.7	14188.2	2.586
H_2O	24756	0.8	19804.8	3.609
MeOH	514700	1.0	514700	93.805

Mass out(MeOH+H_2O)=45.005 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	24756	1.4	34658.4	7.585
MeOH	514700	1.0	514700	92.415

AVG. MWt.	37.409 g/g.mole
Moles MeOH out	1.3551 g.mole/hr
Moles MeOH in	1.6234 g.mole/hr
Conversion, X	17.138%
Rate	0.0287 g.moles/hr.g.cat.

CATALYST	:	Pellet, γ-alumina
rpm	:	1600
Temp.	:	231 °C
Mass of cat.	:	9.6887 gram
Actual mass in	:	51.948 g/hr , feed.
Actual mass out	:	42.84 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	7616	1.7	12947	2.417
H_2O	38780	0.8	31024	5.792
MeOH	491710	1.0	491710	91.791

Mass out(MeOH+H_2O)=41.805 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	38780	1.4	54292	10.97
MeOH	491710	1.0	491710	89.03

AVG. MWt.	30.792 g/g.mole
Moles MeOH out	1.22 g.mole/hr
Moles MeOH in	1.6234 g.mole/hr
Conversion, X	24.685%
Rate	0.04136 g.moles/hr.g.cat.

CATALYST	:	Pellet, γ-alumina
rpm	:	1600
Temp.	:	241°C
Mass of cat.	:	9.6887 gram
Actual mass in	:	51.948 g/hr , feed.
Actual mass out	:	40.86 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	11095	1.7	18861.5	3.586
H_2O	52227	0.8	41781.6	7.944
MeOH	465340	1.0	465340	88.47

Mass out(MeOH+H_2O)=39.395 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	52227	1.4	73117.8	15.458
MeOH	399060	1.0	399060	86.515

AVG. MWt.	35.467 g/g.mole
Moles MeOH out	1.1311 g.mole/hr
Moles MeOH in	1.6234 g.mole/hr
Conversion, X	31.318%
Rate	0.052475 g.moles/hr.g.cat.

CATALYST	:	Pellet, γ-alumina
rpm	:	1600
Temp.	:	251°C
Mass of cat.	:	9.6887 gram
Actual mass in	:	51.948 g/hr , feed.
Actual mass out	:	37.93 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	8875	1.7	15087.5	2.662
H_2O	76333	0.8	61066.4	10.78
MeOH	490520	1.0	490520	86.558

Mass out(MeOH+H_2O)=36.92 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	76333	1.4	106866.2	21.590
MeOH	490520	1.0	490520	78.410

AVG. MWt.	30.161 g/g.mole
Moles MeOH out	1.0051 g.mole/hr
Moles MeOH in	1.6234 g.mole/hr
Conversion, X	38.085%
Rate	0.063812 g.moles/hr.g.cat.

CATALYST	:	-20+30 mesh, γ-alumina
rpm	:	1600
Temp.	:	200 °C
Mass of cat.	:	5.88 gram
Actual mass in	:	30.93 g/hr , feed.
Actual mass out	:	29.00 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	2492	1.7	4236.4	0.849
H_2O	6999	0.8	5599.2	1.122
MeOH	489360	1.0	489360	98.029

Mass out(MeOH+H_2O)=28.754 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	6999	1.4	9798.6	1.963
MeOH	489360	1.0	489360	98.037

AVG. MWt.	31.725 g/g.mole
Moles MeOH out	0.8886 g.mole/hr
Moles MeOH in	0.9666 g.mole/hr
Conversion, X	8.071 %
Rate	0.01327 g.moles/hr.g.cat.

CATALYST	:	-20+30 mesh,γ-alumina
rpm	:	1600
Temp.	:	211 °C
Mass of cat.	:	5.88 gram
Actual mass in	:	30.93 g/hr , feed.
Actual mass out	:	27.54 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	4235	1.7	7199.5	1.267
H_2O	14126	0.8	11330.8	1.989
MeOH	549610	1.0	549610	96.744

Mass out(MeOH+H_2O)=27.191 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	14126	1.4	19776.4	3.473
MeOH	549610	1.0	549610	96.527

AVG. MWt.	31.514 g/g.mole
Moles MeOH out	0.8329g.mole/hr
Moles MeOH in	0.9666 g.mole/hr
Conversion, X	13.833%
Rate	0.0227 g.moles/hr.g.cat.

CATALYST	:	-20+30 mesh,γ-alumina
rpm	:	1600
Temp.	:	221°C
Mass of cat.	:	5.88 gram
Actual mass in	:	30.93 g/hr , feed.
Actual mass out	:	26.58 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	5096	1.7	8663.2	1.716
H_2O	20103	0.8	16082.4	3.186
MeOH	480020	1.0	480020	95.098

Mass out(MeOH+H_2O)=26.124 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	20103	1.4	28144.2	5.538
MeOH	480020	1.0	480020	94.462

AVG. MWt.	31.788 g/g.mole
Moles MeOH out	0.7903 g.mole/hr
Moles MeOH in	0.9666 g.mole/hr
Conversion, X	18.236%
Rate	0.02998g.moles/hr.g.cat.

CATALYST	:	-20+30 mesh, γ-alumina
rpm	:	1600
Temp.	:	231 °C
Mass of cat.	:	5.88 gram
Actual mass in	:	30.93 g/hr , feed.
Actual mass out	:	25.5 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	6427	1.7	10925.9	2.009
H_2O	35216	0.8	28172.8	5.180
MeOH	504800	1.0	504800	92.811

Mass out(MeOH+H_2O)=24.988 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	35216	1.4	49302.4	8.659
MeOH	504800	1.0	504800	91.341

AVG. MWt.	30.711 g/g.mole
Moles MeOH out	0.741g.mole/hr
Moles MeOH in	0.9666 g.mole/hr
Conversion, X	23.312%
Rate	0.03832 g.moles/hr.g.cat.

CATALYST	:	-20+30 mesh, γ-alumina
rpm	:	1600
Temp.	:	241°C
Mass of cat.	:	5.88 gram
Actual mass in	:	30.938 g/hr , feed.
Actual mass out	:	23.3 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	4051	1.7	6886.7	1.263
H_2O	56450	0.8	45160.0	8.307
MeOH	491620	1.0	491620	90.430

Mass out(MeOH+H_2O)=23.005 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	56450	1.4	79030.0	15.83
MeOH	491620	1.0	491620	84.17

AVG. MWt.	31.367 g/g.mole
Moles MeOH out	0.6593 g.mole/hr
Moles MeOH in	0.9666 g.mole/hr
Conversion, X	31.791%
Rate	0.052258 g.moles/hr.g.cat.

CATALYST	:	-20+30 mesh, γ-alumina
rpm	:	1600
Temp.	:	251°C
Mass of cat.	:	5.88 gram
Actual mass in	:	30.938 g/hr , feed.
Actual mass out	:	22.74 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	5625	1.7	9562.50	1.671
H_2O	80701	0.8	64560.8	11.28
MeOH	498000	1.0	498000	87.103

Mass out(MeOH+H_2O)=22.36 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	80701	1.4	112981.4	19.84
MeOH	498000	1.0	498000	80.160

AVG. MWt.	29.654 g/g.mole
Moles MeOH out	0.6146 g.mole/hr
Moles MeOH in	0.9666 g.mole/hr
Conversion, X	36.415%
Rate	0.05986 g.moles/hr.g.cat.

APPENDIX 3

Rate Calculations for The Minimum stirring Speed Test

CATALYST	:	-20+30 mesh γ-alumina
rpm	:	1620
Temp.	:	350 °C
Mass of cat.	:	6.1 gram
Actual mass in	:	30.93 g/hr , feed.
Actual mass out	:	13.4 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	1012	1.7	1720.4	0.344
H_2O	226740	0.8	181392	36.24
MeOH	317410	1.0	317410	63.42

Mass out(MeOH+H_2O)=13.354 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	226740	1.4	317436	50.0
MeOH	317410	1.0	317410	50.0

AVG. MWt.	25 g/g.mole
Moles MeOH out	0.2671 g.mole/hr
Moles MeOH in	0.9666 g.mole/hr
Conversion, X	72.37 %
Rate	0.1147 g.moles/hr.g.cat.

CATALYST	:	-20+30 mesh γ-alumina
rpm	:	1510
Temp.	:	350 °C
Mass of cat.	:	6.1 gram
Actual mass in	:	30.93 g/hr , feed.
Actual mass out	:	13.32 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	1276	1.7	2169.2	0.386
H_2O	251030	0.8	200824	35.72
MeOH	359190	1.0	359190	63.89

Mass out(MeOH+H_2O)=13.269 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	251030	1.4	351442	49.45
MeOH	359190	1.0	359190	50.55

AVG. MWt.	25.076 g/g.mole
Moles MeOH out	0.2674 g.mole/hr
Moles MeOH in	0.9666 g.mole/hr
Conversion, X	72.33 %
Rate	0.1146 g.moles/hr.g.cat.

CATALYST	:	-20+30 mesh γ-alumina
rpm	:	1330
Temp.	:	350 °C
Mass of cat.	:	6.1 gram
Actual mass in	:	30.93 g/hr , feed.
Actual mass out	:	13.58 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	1018	1.7	1730.6	0.317
H_2O	232400	0.8	185920	34.06
MeOH	358240	1.0	358240	65.62

Mass out(MeOH+H_2O)=13.537 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	232400	1.4	325360	47.6
MeOH	358240	1.0	358240	52.4

AVG. MWt.	25.337 g/g.mole
Moles MeOH out	0.28 g.mole/hr
Moles MeOH in	0.9666 g.mole/hr
Conversion, X	71.032%
Rate	0.1126 g.moles/hr.g.cat.

CATALYST	:	-20+30 mesh γ-alumina
rpm	:	1165
Temp.	:	350 °C
Mass of cat.	:	6.1 gram
Actual mass in	:	30.93 g/hr , feed.
Actual mass out	:	13.90 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	1050	1.7	1785.	0.315
H_2O	235290	0.8	188232	33.18
MeOH	377250	1.0	377250	66.50

Mass out(MeOH+H_2O)=13.856 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	235290	1.4	329406	46.61
MeOH	377250	1.0	377250	53.39

AVG. MWt.	25.474 g/g.mole
Moles MeOH out	0.29 g.mole/hr
Moles MeOH in	0.9666 g.mole/hr
Conversion, X	69.957%
Rate	0.1108 g.moles/hr.g.cat.

CATALYST	:	-20+30 mesh γ-alumina
rpm	:	950
Temp.	:	350 °C
Mass of cat.	:	6.1 gram
Actual mass in	:	30.93 g/hr , feed.
Actual mass out	:	14.26 g/hr , product.

Component	GC Area	R.F(wt%)	Corr. Area	Wt%
DME	813	1.7	1382.1	0.242
H_2O	214120	0.8	171296	29.96
MeOH	399060	1.0	399060	69.8

Mass out(MeOH+H_2O)=14.226 g/hr

DME Free Basis:

Component	GC Area	R.F(mol%)	Corr. Area	Mol.%
H_2O	214120	1.4	299768	42.9
MeOH	399060	1.0	399060	57.1

AVG. MWt.	25.995 g/g.mole
Moles MeOH out	0.3125 g.mole/hr
Moles MeOH in	0.9666 g.mole/hr
Conversion, X	67.669%
Rate	0.1072 g.moles/hr.g.cat.

APPENDIX 4

Data on the Acid Catalysts

Catalyst	: γ-Alumina ; Pellet
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 250°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 95.7 %

Comp.	Mean GC Area	Calculated Mole % ‡
Anisole	46702	11.006
Phenol	282080	79.234
O-cresol	31787	7.583
2,6-Xylenol	9462	2.177
2,4,6-Trimethylphenol	0	0

Activity*	: 20.77 %
Selectivity*	: 53.000 %

* Water and methanol-free basis

‡ Product composition

Catalyst	: γ-Alumina ; Pellet
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 300° C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 96.7 %

Comp.	Mean GC Area	Calculated Mole % ‡
Anisole	19383	5.263
Phenol	206160	66.725
O-cresol	56606	15.560
2,6-Xylenol	39605	10.500
2,4,6-Trimethylphenol	8578	1.951

Activity*	: 33.275 %
Selectivity*	: 15.817 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: γ-Alumina ; Pellet
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 350°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 96.9 %

Comp.	Mean GC Area	Calculated Mole % ‡
Anisole	11466	3.197
Phenol	204590	67.988
O-cresol	61328	17.309
2,6-Xylenol	39605	8.877
2,4,6-Trimethyl-phenol	11261	2.629

Activity*	: 32.012 %
Selectivity*	: 9.987 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: γ-Alumina ; -20+30 Mesh
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 250°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 97.7 %

Comp.	Mean GC Area	Calculated Mole % ‡
Anisole	46454	11.937
Phenol	246420	75.471
O-cresol	35986	9.361
2,6-Xylenol	12880	3.231
2,4,6-Trimethylphenol	0	0

Activity*	: 24.53 %
Selectivity*	: 48.665 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: γ-Alumina ; -20+30 Mesh
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 300°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 96.6 %

Comp.	Mean GC Area	Calculated Mole % ‡
Anisole	14406	4.141
Phenol	192660	66.005
O-cresol	54667	15.906
2,6-Xylenol	40126	11.261
2,4,6-Trimethylphenol	11162	2.687

Activity*	: 33.995 %
Selectivity*	: 12.181 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: γ-Alumina ; -20+30 Mesh
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 350°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	:1700
Mass balance closure	: 96.5 %

Comp.	Mean GC Area	Calculated Mole % ‡
Anisole	12905	3.238
Phenol	228940	68.478
O-cresol	71672	18.207
2,6-Xylenol	29946	7.337
2,4,6-Trimethylphenol	13034	2.739

Activity*	: 31.522 %
Selectivity*	: 10.272 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 0.5 P/Al (-14+20 Mesh)
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 250°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 96.0 %

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	73420	18.16
Phenol	235070	69.32
O-cresol	36231	9.07
2,6-Xylenol	14231	3.44
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 30.7 %
Selectivity*	: 59.28 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 0.5 P/Al (-14+20 Mesh)
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 280°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 97.9 %

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	25648	14.37
Phenol	101580	67.82
O-cresol	21805	12.36
2,6-Xylenol	9972	5.45
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 32.18%
Selectivity*	: 44.66 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 0.5 P/Al (-14+20 Mesh)
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 300°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 98.9 %

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	24244	12.40
Phenol	110890	67.63
O-cresol	27397	14.19
2,6-Xylenol	11565	5.78
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 32.40%
Selectivity*	: 38.27 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 0.5 P/Al (-14+20 Mesh)
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 350°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 98.8 %

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	6190	7.81
Phenol	46090	62.28
O-cresol	14166	18.09
2,6-Xylenol	3916	4.82
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 30.70%
Selectivity*	: 25.41 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 0.8 P/Al (-14+20 Mesh)
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 250°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 98.4 %

Comp.	Mean GC Area	Calculated MOLE %‡
Anisole	65885	18.57
Phenol	208090	69.91
O-cresol	30111	8.59
2,6-Xylenol	10623	2.92
2,4,6-Trimethyl-phenol	0.0	0.0

Activity*	: 30.10%
Selectivity*	: 61.79 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 0.8 P/Al (-14+20 Mesh)
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 280°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balabnce closure	: 98.5 %

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	31918	15.47
Phenol	118430	68.42
O-cresol	23893	11.72
2,6-Xylenol	9278	4.39
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 31.58 %
Selectivity*	: 48.99 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 0.8 P/Al (-14+20 Mesh)
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 300°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 99.0 %

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	28202	13.91
Phenol	117470	69.05
O-cresol	25325	12.64
2,6-Xylenol	9139	4.40
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 31.00 %
Selectivity*	: 44.84 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 0.8 P/Al (-14+20 Mesh)
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 350°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 98.8 %

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	15030	9.24
Phenol	97807	71.71
O-cresol	23803	14.82
2,6-Xylenol	7031	4.22
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 28.30 %
Selectivity*	: 32.51 %

‡ Product composition

* Water and methanol-free basis

Appendix 5

Data on the Base Catalyst

Catalyst	: 10 % Na_2HPO_4 (-14+20 Mesh)
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 250°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 97.34%

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	1357	0.297
Phenol	391270	99.703
O-cresol	0.0	0.0
2,6-Xylenol	0.0	0.0
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 0.297 %
Selectivity*	: 100.0 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 10 % Na_2HPO_4 (-14+20 Mesh)
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 300°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 97.56%

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	7535	1.668
Phenol	372570	98.332
O-cresol	0.0	0.0
2,6-Xylenol	0.0	0.0
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 1.668 %
Selectivity*	: 100.0 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 10 % Na_2HPO_4 (-14+20 Mesh)
WHSV	: 5.0
Pressure	: 5.0 psig
Temperature	: 350°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 96.68%

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	19846	4.686
Phenol	337580	95.008
O-cresol	0.0	0.0
2,6-Xylenol	0.0	0.0
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 4.992 %
Selectivity*	: 93.87 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 10 % Na_2HPO_4 (-14+20 Mesh)
WHSV	: 1.7
Pressure	: 5.0 psig
Temperature	: 350°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 98.16%

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	50583	10.45
Phenol	358680	88.33
O-cresol	5837	1.22
2,6-Xylenol	0.0	0.0
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 12 %
Selectivity*	: 90 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 10 % Na_2HPO_4 (-14+20 Mesh)
WHSV	: 3.64
Pressure	: 5.0 psig
Temperature	: 350° C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 97.50%

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	25809	5.81
Phenol	347310	93.66
O-cresol	2186	0.501
2,6-Xylenol	0.0	0.0
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 6 %
Selectivity*	: 92 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 10 % Na_2HPO_4 (-14+20 Mesh)
WHSV	: 7.3
Pressure	: 5.0 psig
Temperature	: 350° C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 98.69%

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	10078	2.32
Phenol	355430	97.68
O-cresol	0.0	0.0
2,6-Xylenol	0.0	0.0
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 2 %
Selectivity*	: 100 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 20 % Na_2HPO_4 (-14+20 Mesh)
WHSV	: 1.70
Pressure	: 5.0 psig
Temperature	: 350°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 96.99 %

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	54856	11.32
Phenol	355080	87.36
O-cresol	65310	1.32
2,6-Xylenol	0.0	0.0
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 13 %
Selectivity*	: 90 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 20 % Na_2HPO_4 (-14+20 Mesh)
WHSV	: 3.34
Pressure	: 5.0 psig
Temperature	: 350°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 97.85 %

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	37241	8.24
Phenol	345400	91.14
O-cresol	2738	.61
2,6-Xylenol	0.0	0.0
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 9 %
Selectivity*	: 93 %

‡ Product composition

* Water and methanol-free basis

Catalyst	: 20 % Na_2HPO_4 (-14+20 Mesh)
WHSV	: 6.94
Pressure	: 5.0 psig
Temperature	: 350°C
Phenol/MeOH (molar ratio)	: 1/2
RPM	: 1700
Mass balance closure	: 97.19 %

Comp.	Mean GC Area	Calculated Mole %‡
Anisole	24357	5.36
Phenol	359600	94.33
O-cresol	1393	.31
2,6-Xylenol	0.0	0.0
2,4,6-Trimethylphenol	0.0	0.0

Activity*	: 6 %
Selectivity*	: 94.3 %

‡ Product composition

* Water and methanol-free basis

APPENDIX 6

Equilibrium Calculation

EQUILIBRIUM CALCULATIONS

1. Benson Method :

1. Anisole :

Group	ΔH_{298} (kcal/mol)	S^{o}_{298} (cal/mol.k)	C_p (cal/mol.k) 300K	400K	500K	600K	800K
5 (C_B-H)	16.50	57.65	16.20	22.20	27.30	31.50	37.70
C_B-O	-0.90	-10.20	3.9	5.3	6.2	6.6	6.9
O-(C_B)C	-22.6	10.1	3.4	3.7	3.7	3.7	4.4
C-(O)$(H)_3$	-10.1	30.41	6.19	7.84	9.40	10.79	13.03
R ln 6	0.0	-3.55	--	--	--	--	--
	-------	-------	------	------	------	------	------
	-17.1	84.4	26.69	39.04	46.60	52.59	62.03

$$\Delta C_p^{\circ}\,rxn = (\,C_p^{\circ}\,anisole + C_p^{\circ}\,water\,) - (\,C_p^{\circ}\,phenol + C_p^{\circ}\,MeOH\,)$$

Component	C_p (cal/mol.k) 300K	400K	500K	600K	800K
Anisole	26.69	39.04	46.60	52.59	62.03
Water	8.03	8.19	8.42	8.68	9.25
MeOH	10.52	12.29	14.22	16.02	19.04
Phenol	24.90	32.45	38.64	43.54	50.62
	------	------	------	------	------
$\Delta C_p^{\circ}\,rxn$	-0.700	+2.490	+2.160	+1.710	+1.620

$$\Delta C_{pmean} = 0.5 (\Delta C_{pT1} + \Delta C_{pT2})$$

Temperature(K)	ΔC_{pmean}
300	-0.700
400	0.895
500	2.325
600	1.935
800	1.665

$$\Delta S^{\circ}_{f(298)} = S^{\circ}_{products} - S^{\circ}_{reactants}$$
$$= (84.4 - 45.11) - (75.43 + 57.29) = -93.43$$
$$\Delta S_{fT} = \Delta S_{f298} + \Delta C_{pmean} * \ln (T/298)$$

Temperature(K)	ΔS_{fT}
300	-93.43
400	-93.17
500	-92.23
600	-92.08
800	-91.78

$$\Delta H^{o}_{fT} = \Delta H_{f298} + C_{pmean} * (T_T - 298)$$

Temperature(K)	ΔH_{fT}
300	-17.10
400	-17.01
500	-16.63
600	-16.52
800	-16.43

$$\Delta G_{fT\ anisole} = \Delta H_{fT} - T * \Delta S_{fT}$$

Temperature(K)	$\Delta G_{fT\ anisole}$
300	10.930
400	20.258
500	29.485
600	38.730
800	56.990

2. Van Krevelen Method : (300 - 600 K)

Group	A	B
HC ⇔	5*3.047	$5*0.615*10^{-2}T$
-C ⇔	4.675	$1.150*10^{-2}T$
-O-	-15.79	$-0.85*10^{-2}T$
$-CH_3$	-10.943	$2.215*10^{-2}T$
R ln σ	-------	$0.356*10^{-2}T$
---------	---------	----------
Total Contribution	-6.823	$+5.946*10^{-2}T$

Temperature(K)	ΔG_{fT} anisole
300	11.015
400	16.961
500	22.907
600	28.853

Summary :

$\Delta G_{rxn} = \Delta G_{products} - \Delta G_{reactants}$

1. Anisole reaction based on Benson method :

Temperature(K)	ΔG_{rxn} (Kcal/mole)	$K_{equilibrium}$
300	10.930	0.00825
400	20.258	0.00245
500	29.485	0.00170
600	38.730	0.00190
800	56.990	0.00288

2. Cresol reaction based on tabulated data :

Temperature(K)	ΔG_{rxn} (Kcal/mole)	$K_{equilibrium}$
300	-16.79	$1.71*10^{12}$
400	-16.64	$1.24*10^{09}$
500	-16.55	$1.72*10^{07}$
600	-16.54	$1.06*10^{06}$
800	-16.56	$3.34*10^{04}$