Introduction

Since 1982, Air Products and Chemicals, Inc., with support from the U. S. Department of Energy, has been developing reaction technology based on the conversion of coal-derived synthesis gas in a liquid-phase process. The liquid-phase reactor operates by bubbling the synthesis gas up through an inert mineral oil containing a powdered catalyst. This mineral oil provides excellent temperature control allowing for isothermal operation. The scope of this work has involved several major objectives. The first objective was to develop a liquid-phase process to produce methanol (LPMeOH) This process was designed as a once through reactor for incorporation into coal gasification combined cycle (CGCC) plants where it would be used to produce methanol from the synthesis gas during off-peak hours. Stored methanol could then be used for power production during peak hours allowing the size of the gasification unit to be reduced.

A second objective was to extend the methanol technology to produce dimethyl ether (LPDME) by dehydration of the methanol in a single reactor. The synthesis of DME leads to higher syngas conversion per pass than methanol equilibrium. DME synthesis has importance as a chemical building block and as a potential oxygenated additive to the transportation fuel market.

The current objective is stated under sub task 3.1 in the April 1990 Alternate Fuels Proposal to the Department of Energy (RFP # DE-RP22-90PC90018). It involves developing new technology, based on the liquid-phase process, for conversion of coal-derived synthesis gas to oxygenated hydrocarbon fuels, fuel additives, and fuel intermediates. These oxygenates consist of higher alcohols and ethers which possess high octane numbers and can be used as additives to current fuel mixtures.

One such ether currently being used in transportation fuel is methyl tertiary-butyl ether (MTBE). Recent research in the Process Systems Group has focused on the synthesis of MTBE from syngas using liquid phase technology. This work has progressed in two separate stages. The first consists of developing the process for producing isobutanol directly from synthesis gas. This work has focused on defining a catalyst system and operating conditions which yield high selectivities of branched higher alcohols, namely isobutanol. Equilibrium concentration of methanol, which can serve as a feed stock for MTBE production, is also produced in this process.

The second stage consists of establishing the use of a liquid phase reactor for dehydration of the isobutanol to isobutene. This entails the development of a catalyst system and reaction conditions which provide high conversion of the alcohol and high selectivity for the branched olefin. Production of MTBE from isobutene and methanol is well known technology.

Because of increasing environmental concerns throughout the world, the demand for MTBE as an oxygenated fuel additive has increased dramatically over the past few years. Currently, the major source of isobutene is the C4 fraction from steam cracking or catalytic cracking.[1] A fraction of the isobutene supply is obtained from the dehydration of tertiary-butyl alcohol (TBA). TBA is a major byproduct in the manufacture of propylene oxide from propylene and tertiary hydroperoxide.[2] Due to limited capacities of these sources, the increasing demand for MTBE is predicted to cause a short-fall in the near future. Technology that is currently being implemented to supplement the capacity of isobutene consists of a two stage process whereby normal butane is isomerized into isobutane which is then dehydrogenated to produce isobutene. This technology establishes the benchmark for the liquid phase process. If proven economically viable, the liquid phase technology will provide the ability to produce isobutene from coal and natural gas thereby expanding the sources of this important chemical.

This report describes the initial results of the exploratory investigations in the use of a liquid phase reactor for the conversion of isobutanol to isobutene. Also included is a survey of the prior knowledge associated with the dehydration of higher alcohols.

Objectives

The overall objective of this research program was to develop a slurry reactor based process for the dehydration of isobutanol to isobutene. The specific objectives were:

(1.) To screen catalysts for dehydration of isobutanol.
(2.) To define operating conditions which provide high conversion of isobutanol to isobutene.
(3.) To minimize isomerization of the branched structure upon dehydration.

Summary and Conclusions

Experiments were performed in a 300 cc autoclave reactor to evaluate the use of a liquid phase reactor process for the dehydration of isobutanol. The primary product of the dehydration is isobutene which can serve as a feed stock for methyl tertiary-butyl ether (MTBE) production. Alumina catalysts were chosen for the investigation because of their wide use as a dehydration catalyst. Four commercially available alumina catalysts were evaluated for both activity and selectivity to the branched olefin.

All four catalysts demonstrated high conversions (>80%) at temperatures of 290 °C and a pressure of 150 psig. Conversions of near 100% could be obtained at 330 °C. Increased pressure had a detrimental effect on the isobutanol conversion. The reactor feed consisted of 5 mol% isobutanol in nitrogen. As the GHSV was increased from 1200 to 6000 sl/kg-hr (60 to 300 sl/kg-hr based on isobutanol), the isobutanol conversion decreased from 17.7 to 35.9% for the alumina catalysts.

A yield of 0.90 mole isobutene per mole reacted isobutanol or better was obtained at conversions of 60-70% and higher for all four catalysts. From 75 to 98% conversion, the four catalysts all provide an isobutene yield ranging from 0.92 to 0.94 with the maximum occurring at about 90% conversion. At conversions lower than 90%, the concentration of diisobutyl ether increases significantly with decreasing conversion. The concentration of linear butenes is essentially a linear function of conversion up to 98% where it begins to rise rapidly. Formation of the isobutene occurs through a concerted (E2) mechanism involving an adsorbed alcohol molecule. Diisobutyl ether is formed by reaction of a surface alkoxide with an adsorbed alcohol. The mechanism of linear butene formation is uncertain. They may be formed by re-adsorption of the isobutene and secondary isomerization, primary isomerization during the dehydration step, or from decomposition of the ether.

Doping of the catalyst with up to 0.8 wt.% potassium showed a modest increase in isobutene selectivity. The increase was proportional to the potassium loading up to 0.5 wt.%. A weight loading greater than 0.5% did not provide any further increase in selectivity. This increase in isobutene selectivity, however, was more than offset by a reduction in activity resulting in substantially lower yields. Investigations using a mixed alcohols feed (consistent with that produced in isobutanol synthesis from syngas) demonstrated a small increase in the selectivity of the C4 iso-olefin over that observed for a pure isobutanol feed.

The dehydration reaction was modeled using a simple power law expression. The effects of water and isobutene were separated through experiments using a mixture of isobutanol and water. The rate of isobutanol dehydration is essentially first order in alcohol and is a strong inverse function of the concentration of water present in the reactor. The power law expression provided a good correlation to the experimental data.

Patent Situation

The following idea proposal was submitted:

> "A Novel Isobutanol Dehydration Catalyst Derived From Hydrotalcite-Type Anionic Clay", I-C2818, 29 April 1992.

The idea proposal was dropped from the committee because experiments in a packed bed reactor showed poor performance for both isobutanol conversion and isobutene selectivity.

Safety

The primary hazards associated with this experimental study were the flammability of isobutene and isobutanol. The source of isobutanol was the liquid injection pump. The volume of the pump was small enough to maintain the concentration below flammability limits even in the event of a hood failure. Gloves, safety glasses, and lab coat were worn during filling of the pump to guard against contact.

Isobutene originated from dehydration of the isobutanol and from isobutene standards used for calibration of the GC. The standards were fitted with restrictor valves to minimize flow. The experimental apparatus was contained in a ventilated enclosure equipped with a flammable monitor which was interfaced to the reactor system allowing for automatic shutdown.

Regulatory Matters

1,3 butadiene is an OSHA regulated suspect carcinogen. This chemical is present in minute quantities in the product stream. Enclosure of the apparatus in the ventilation system and venting of reaction products to the atmosphere prevented accumulation.

Future Programs

Further investigations of the process developed in this report will focus on high isobutanol feed concentrations approaching pure isobutanol. This technology is scheduled for a demonstration run at the AFDU at LaPorte in late summer 1993. Another area of future consideration is development of a catalyst which inhibits isomerization of the branched carbon structure while maintaining high activity for the dehydration reaction.

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1. Literature Review

A literature review was conducted in the initial stage of this project. The initial literature search was performed on "dehydration of isobutanol". Chem Abstracts was searched from 1967 to present. Limited information prompted an expanded search on the dehydration of alcohols, specifically those with similar structure, i.e. 2-methyl-1-alkanols. This information was summarized in a memo dated 24 March 1992 and is included in Appendix I. Several patents concerned with dehydration of tertiary butanol were obtained after distribution of the memo and will be discussed briefly due to their importance in the development of a new process for the dehydration of isobutanol.

Prior art for the dehydration of tertiary butanol involved conventional batch methods wherein the water formed during the reaction had a detrimental effect on the reaction rate. This process used ion exchange resins dispersed in an alcohol-water mixture which initially contained up to 20-30 wt.% water. Process temperatures were 70-100 °C at pressures around atmospheric producing isobutene as an overhead gas.[3]

An Atlantic Richfield patent disclosed a continuous dehydration process in which water formed in the reaction was removed by azeotrope formation with benzene.[3] A cation exchange resin, in particular, the sulfonic acid type was used with the amount of benzene ranging from 2 to 20 times the weight of catalyst. Temperatures of 70 to 90 °C were used with the isobutene and benzene-water azeotrope removed overhead. The benzene-water azeotrope was condensed and allowed to separate into two phases, a hydrocarbon and an aqueous phase. The hydrocarbon was recycled maintaining the concentration of benzene approximately constant in the reactor. Reaction rates 10 times higher than those of the batch methods were obtained. The authors claimed that the isobutene purity was much higher compared to product spectrums from sulfuric acid and high temperature vapor phase catalytic dehydrations. Temperatures greater than 100 °C were avoided to prevent dimerization of the isobutene.

A Cities Service patent expanded on this technology by placement of the alcohol feed at the three phase separator.[4] With this configuration, a wet tertiary butanol feed was dried significantly before entering the dehydrator. The feed alcohol dissolved in the hydrocarbon phase causing most of the feed water to enter the aqueous phase. The hydrocarbon phase was then pumped back to the reactor providing the dry alcohol feed as well as the azeotrope forming hydrocarbon. This process provided an inexpensive means to dry a typical feed stream which may contain up to 60 wt.% water. Analysis of the mixed xylene solution (azeotrope forming hydrocarbon) showed 40% of the xylenes underwent butylation. This alkylation is undesirable because it changes the character of the azeotrope forming mixture and also consumes alcohol.

Another patent issued to Cities Service described the use of a liquid catalyst, para-toluenesulfonic acid, dissolved in a mixed xylene solvent.[5] This catalyst overcomes the problem of catalyst attrition affiliated with the particulate ion exchange resins. Temperatures up to 200 °C may be used providing higher reaction rates. Above 200 °C, significant dimerization of isobutene occurred. Butylation of the mixed xylene solvent was still a problem. Paraxylene, which is more expensive than mixed xylenes, did not undergo butylation.

A Nippon Oil patent disclosed a process for dehydration of tertiary butanol whereby water present in the reactor from both the feed and as a reaction product was withdrawn from the bottom of the reactor.[6] This process used a cation exchange resin catalyst dispersed in an alcohol-water mixture. The liquid mixture contained 10-60 wt.% alcohol. Reaction temperatures ranged from 90-180 °C with elevated pressures to maintain the alcohol-water mixture as a liquid. The feed was introduced to the reactor as a gas at a level 1/2 to 9/10 below the top of the liquid mixture. Overhead from the reactor contained isobutene and unreacted alcohol. A bottoms stream was withdrawn to remove the water. This bottoms stream must be distilled to recover unreacted alcohol significantly increasing the cost of the process.

A German patent issued to BASF discussed a process for the dehydration of alcohols where the catalyst was dispersed in a high-boiling mineral oil.[7] The authors claim that both soluble and insoluble acid catalysts could be used; however, data are shown for only one catalyst, dodecylbenzosulfonic acid. Suggested reactors for this process include bubble cap columns, bubble towers, and packed columns. In this process, liquid or gaseous alcohol is fed into the bottom of the reactor. The reactor is operated at temperatures above the boiling point of the feed. The product stream is withdrawn overhead containing olefin, water, and unreacted alcohol. Benefits of this process include use of soluble catalysts as well as good temperature control.

While the BASF patent discloses a process which parallels the one described in this report, it fails to address a critical issue with regard to the dehydration of branched alcohols, namely rearrangement of the branched structure. Only limited data was presented for tertiary butanol, cyclohexanol, and 1-butanol. The dehydration of 1-butanol resulted in a yield of only 86% 1-butene with the remainder consisting of the 2-butenes. Thus, the issues to be addressed include determination of a catalyst and process conditions which provide high yields of the branched olefin as well as scaling up the process for commercialization.

2. Thermodynamics of Isobutanol Dehydration to Isobutene

Thermodynamic calculations were performed on the dehydration reactions for isobutanol and tert-butanol to isobutene and water (Appendix II). At equilibrium, isobutanol has a higher conversion than tert-butanol at all the reaction conditions calculated. The difference becomes more pronounced at lower temperatures where only about 50% of the tert-butanol is converted. Isobutanol is essentially completely converted at temperatures from 100 to 300 °C and pressures from 1 to 52 atm.

An endothermic heat of reaction of 6.4 kcal/gmol was calculated for the dehydration of isobutanol. Using this value, adiabatic temperature drops were calculated to determine the plausibility of performing this reaction in an adiabatically operated packed bed reactor (Appendix II). The temperature drop is quite large (130 to 170 °C) and presents the possibility of formation of a liquid phase at higher conversions. This large temperature drop makes an adiabatically operated packed bed reactor unfavorable, thus providing the incentive to investigate the use of a liquid phase reactor for the dehydration of isobutanol. Advantages of a liquid phase reactor over a packed bed with interstage heating are simplicity of design and operation and isothermal temperature control.

3. Experimental

The experiments were conducted in a mechanically stirred 300 cc autoclave reactor (Autoclave Engineers). The reactor unit was operated in a continuous once-through mode. Specific details of the unit are given in the hazards review.[8] A simplified schematic of the equipment is shown in Figure 3.1.

The slurrying liquid was Drakeol 10, a white mineral oil composed of C16-C38 straight-chain, branched, and naphthenic saturated hydrocarbons. About 30 g of calcined catalyst was mixed with the oil representing a 20 wt.% catalyst loading. The catalysts were calcined at 500°C under a nitrogen atmosphere. Isobutanol was injected into a preheater/vaporizer unit by an Isco high pressure syringe pump. Nitrogen was used as a carrier gas for the vaporized alcohol. Contamination of the vaporizer unit with catalyst from previous experiments prompted removal of the unit and direct injection of the alcohol into the reactor. The alcohol was preheated before entrance into the reactor. A radial flow turbine impeller with a stirring speed of 1200 rpm was used to ensure mass transfer effects were negligible. This was based on LPMEOH and LPDME studies. Exit gases from the reactor passed through a gas-liquid separator where entrained oil was refluxed back to the reactor. The flow rate of the exit stream was measured by a wet test meter. Pressure in the reactor was controlled by a back pressure regulator on the exit line.

The product gas stream was analyzed by on-line gas chromatography. Two Hewlett-Packard 5890 GCs were used. The one contained two Thermal Conductivity Detectors (TCDs), one for detection of N_2 and the other for H_2. The second GC contained two Flame Ionization Detectors (FIDs), one for detection of the unreacted isobutanol and the second for isobutene and the butene isomers. The analytical system is described in more detail in Appendix III.

4. Results and Discussion

4.1 Catalyst Screening

A large number of possible dehydration catalysts obtained from the literature were screened using a packed bed reactor (Fran Waller, CSTC). Those giving the best performance were alumina-based. Synthesis studies of dimethyl ether from syngas also focused on alumina-based dehydration catalysts.[9] Thus, four commercially available alumina catalysts were chosen for screening studies in the 300 cc autoclave to test their use in a bubble column reactor. The catalysts used were Conoco gamma-alumina (Catapal B), LaRoche gamma-alumina (Versal GH), Engelhard gamma-alumina (Al-3996R), and LaRoche eta-alumina (Versal B). Physical property data are listed in Table 4.1.1. The stability of Drakeol 10 oil in the presence of an alumina catalyst was tested at 350 °C with no degradation of the oil observed by GC analysis. Previous experience with Drakeol 10 and an alumina was at temperatures of 250-280 °C.

Experiments were performed using a 5 mol% isobutanol in nitrogen feed with direct injection of the isobutanol into the reactor, thus bypassing the vaporizer. Initial experiments had shown that contamination of the vaporizer from previous usage was causing dehydrogenation of the isobutanol. High concentrations of isobutanol could not be used due to condensation of the product water and unconverted alcohol in the exit stream providing inaccurate GC analysis.

4.1.1 Temperature

The performance of the four catalysts as a function of temperature was investigated for a feed of 5 mol% isobutanol in N2, a pressure of 150 psig, and a GHSV of 2500 sl/kg-hr (Figures 4.1.1 and 4.1.2). The conversions at 330 °C are the same among the catalysts ranging from 98.6 to 99.7% isobutanol conversion. At 290 °C the variability in the catalyst activities is more apparent. The activity for Versal B at 290 °C was that of Versal B doped with 0.2 wt.% potassium. The activity of Versal B was similar to that of Versal B doped with 0.2 wt.% potassium at several other operating conditions and is expected to be so at this condition. Catalyst Al-3996R has a higher activity at 290 °C than the other three catalysts. As the temperature is decreased below 330 °C, all four catalyst demonstrate a decrease in activity, Al-3996R having the smallest followed by Catapal B, Versal GH, and finally Versal B. Below 290 °C, the activity decreases rapidly with temperature indicating that 280-290 °C is the low temperature limit where conversions of 80% or better can still be obtained. This is an important result with regard to implementation of this technology into the DOE's Alternative Fuels Development Unit (AFDU) at LaPorte, Texas. The current temperature limitation of the AFDU is about 300 °C. Because the reaction is endothermic and heat is required to drive the reaction, the highest temperature obtainable during a run may actually be lower than 300 °C which would result in low yields of isobutene

The yield of isobutene, based on converted isobutanol, possesses a maximum at 290 °C for all four catalysts. While data at lower temperatures than 290°C is not available for Versal GH and Al-3996R, it is believed that they exhibit a true maximum in isobutene yield around 290 °C. Further evidence of this will be discussed in a later section. Below 290 °C, Catapal B and Versal B demonstrate a sharp decrease in isobutene yield with decreasing temperature, while above 290 ° C, all four catalysts show a more gradual decline in yield. Figure 4.1.2 illustrates the yields of linear butenes and diisobutyl ether as a function of temperature for the four catalysts. For temperatures below 290 °C, the yield of ether increases substantially leading to the sharp decrease in the yield of isobutene. At a temperature of 250 °C, diisobutyl ether can represent 20-30 wt.% of the organics. As the temperature is raised, the yield of ether drops toward zero. However, the concentration of linear butenes increases almost linearly with temperature causing the yield of isobutene to decrease at higher temperatures. Therefore, the optimum yield of isobutene appears to be a function of competing mechanisms.

It is believed that the dehydration of isobutanol occurs via an E2 reaction mechanism which involves a single transition state. The mechanism involves the abstraction of the β-hydrogen of the alcohol by a surface oxide ion with simultaneous cleavage of the alcohol hydroxyl group forming water and a surface oxide ion.[9] An E1 mechanism involves cleavage of the hydroxyl ion to form a carbonium ion in the first step. In the second step the carbonium ion losses a proton to the base to form the alkene. In kinetic isotope studies, Knozinger and Scheglila[10] found the largest isotope effect occurred for β-carbon deuteration of isobutanol while having only a small effect on tertiary butanol, thus establishing the E2 mechanism for isobutanol.

According to Pines and Haag[9] as well as Knozinger and Scheglila[10], pure β-elimination occurs to form the primary dehydration product, the olefin. This olefin product may then re-adsorb onto strong acid sites where it may undergo isomerization. This would seem consistent with regard to the increase in the concentration of linear butenes with conversion. As the conversion increases, the concentration of isobutene on the surface and in the pores increases presenting a greater probability for re-adsorption. However, if re-adsorption were occurring it is expected that there would also be evidence of oligomerization. Oligomerization would occur because the re-adsorbed isobutene molecules are highly active when undergoing isomerization. According to GC analysis, there was no evidence in any of the dehydration experiments of dimers or trimers of isobutene.

It is also possible that formation of the linear butenes is a direct temperature effect and not necessarily dependent on the concentration of isobutene. One possibility is that the catalyst sites responsible for isomerization have a higher activation energy than the majority of active sites on the catalyst surface. At higher temperatures, a greater proportion of these isomerization sites would be active causing the isobutene selectivity to decrease. Knozinger[11] suggests that instead of re-adsorption of the isobutene, it is possible that at higher temperatures (T>300 °C) γ-H elimination may occur with subsequent migration of the hydrogen or methyl group leading to the linear isomers.

Arai et al.[12] through studies on ethanol dehydration, postulated that ether was formed by reaction of two nearby surface ethoxides. The presence of surface ethoxides was verified through IR studies. Knozinger and Kohne[13] proposed that diethyl ether was formed by reaction of an adsorbed alcohol molecule with a surface ethoxide. They found similar behavior for straight-chained alcohols up to n-hexanol. As the chain length was increased, the temperature range in which ether was the only product decreased. No ether was detected by Knozinger and Kohne as a dehydration product for the branched butanols. They also state that the ether formed undergoes decomposition above a certain temperature to olefin and alcohol or to olefin and water. The temperature of decomposition is dependent on the molecular weight of the ether. de Boer et al.[14] found no evidence of ethylene production from dietheyl ether at low alcohol conversions and suggests both reactions occur simultaneously under dehydration conditions. According to Knozinger and Kohne,[13] at higher temperatures the free energy for olefin formation decreases more rapidly than that of ether causing the shift toward direct olefin formation. Thus, as the temperature is increased, the dehydration mechanism shifts from reaction of a surface alkoxide to a concerted mechanism involving an adsorbed alcohol.

4.1.2 Pressure

The effect pressure has on the reaction is illustrated in Figures 4.1.3 and 4.1.4. Experiments were performed using 5 mol% isobutanol in N_2 and a GHSV of 2500 sl/kg-hr. An increase in pressure from 150 to 500 psig resulted in a decrease of 21.0 and 13.7% in the isobutanol conversion for

Catapal B and Al-3996R at 290 °C. Pressure data is not available for Versal B and Versal GH at 290 °C. Isobutene yield also decreased with an increase in reactor pressure. The isobutene yield with Al-3996R decreased 0.8% and that of Catapal B by 1.6%. This is due to an increase in the concentration of diisobutyl ether at the lower conversions.

As the temperature was increased, the effect pressure had on the conversion became less significant (Figure 4.1.4). At 310 °C Al-3996R showed a 5.0% decrease in conversion with increased pressure, while at 330 °C isobutanol conversion with Catapal B dropped only 0.2%. Thus as the temperature is raised to 330 °C, the reactor pressure becomes insignificant with regard to conversion. The functionality of isobutene yield is more complex. At 250 °C the yield, based on converted isobutanol, decreased 11.2% with increased pressure due to an increased ether concentration. This trend is also seen at 290 °C for both Catapal B and Al-3996R, but to the extent of only 1.4 and 0.6%, respectively. At 310 and 330 °C, the isobutene yield increased with increased pressure which is opposite to the trend at lower temperatures. At these high temperatures, the concentration of ether is insignificant; however, the concentration of linear butenes has proportionally increased causing an affect on isobutene yield. Interestingly, the isobutene yield for catalyst Al-3996R is approximately the same at 290 °C, 150 psig and 310 °C, 500 psig where the conversion is the same. The product compositions were identical except for a trace quantity of diisobutyl ether at 310 °C, 500 psig. This indicates that temperature is not the only factor influencing the reaction mechanism.

The dehydration reaction favors low pressure, which is especially evident at 290 °C. This is an important factor because the second major product of the dehydration reaction is water. Operating at low pressures reduces the temperature constraints necessary to maintain the feed and products in the gas phase. Condensation of water in the reactor unit could lead to catalyst deactivation through re-hydration of the catalyst surface. High pressure also causes a slight increase in the formation of diisobutyl ether.

4.1.3 Gas Hourly Space Velocity

Evaluation of the effect GHSV has on this reaction is more difficult because a feed of only 5 mole percent was being tested. Thus the actual space velocity of isobutanol is much lower than that stated in the figures and tables. The current configuration of the reactor system limits the concentration of isobutanol in the feed due to condensation problems. On a commercial unit the feed would consist of either 100% isobutanol or a mixture of isobutanol and higher carbon number alcohols. Using this feed it is possible to run at low space velocities while still obtaining reasonable productivity. While limited in scope, the experimental results do provide some important information. The experimental conditions were 290 and 330 °C, 150 psig, and 5 mol% isobutanol in N_2.

The GHSV has a significant effect on the isobutanol conversion at 290 °C as is shown in Figure 4.1.5. As the GHSV was increased from 1200 to 6000 sl/kg-hr (60 to 300 sl/kg-hr based on isobutanol), the isobutanol conversion decreased 17.7% for Al-3996R and 35.9% for Versal GH.

The percentage decrease for Catapal B and Versal B was predicted to be 25 and 36%, respectively, based on the data at 2500 and 6000 sl/kg-hr. This trend is not unexpected since the increase in GHSV represents up to a five-fold decrease in the mean residence time of the alcohol in the reactor. Al-3996R demonstrated the best activity over the range of space velocities with the separation in performance increasing with increasing GHSV. Isobutene yield demonstrated the same trends as seen with temperature and pressure. At conversions less than 90% the yield decreased as a result of increased ether formation. This was evident for all of the catalysts. Versal GH had the sharpest decline in isobutene yield due to having the largest drop in conversion. Al-3996R was the only catalyst having conversion data above 90% under these conditions. At a conversion greater than 90% the isobutene yield declined as a result of an increase in the concentration of linear butenes.

At 330 °C, the effect of varying GHSV is less significant (Figure 4.1.6). Al-3996R showed only a 0.6% decline in conversion while Versal GH had a 3.5% decline. Interestingly, all of the catalysts showed a similar slope in the decline in conversion between 2500 and 6000 sl/kg-hr except Al-3996R which showed almost no change in activity. The isobutene yield followed the trend that had been demonstrated in Figure 4.1.5. As the isobutanol conversion decreased from near 100% toward 90%, the yield of isobutene increased due to a decrease in the concentration of linear butenes. At this temperature and these high conversions, diisobutyl ether was nonexistent. Catalyst Al-3996R showed a discrepancy in this trend. It presents a maximum in isobutene yield at a GHSV of 2500 sl/kg-hr even though the conversion is above 99% for all three space velocities. The reason for this is unknown, but thought to be a problem with the GC analysis.

Comparison of Figures 4.1.3 and 4.1.5 indicates that there may be a correlation between the effects pressure and GHSV have on catalyst activity and isobutene yield. An increase in GHSV from 2500 to 6000 sl/kg-hr at 290 °C produced the same decrease in isobutanol conversion for both Al-3996R and Catapal B as did an increase in pressure from 150 to 500 psig. The surprising point is that both variable changes produced almost identical yields of isobutene, ether, and linear butenes given that only the conversion was identical. An increase in reactor pressure has the effect of increasing the partial pressures of isobutanol, isobutene, diisobutyl ether, and water. This would be expected to have an influence on the chemical kinetics and possibly favor the formation of one product over another in simultaneous reactions. Increasing the GHSV causes a decrease in the mean residence time providing less contact time between the alcohol and the catalyst. Therefore, it is not expected that a change in these two variables producing the same degree of alcohol conversion should produce the exact same yield of several products. This result is similar to that mentioned previously where the same yield of products was obtained for two separate runs at different temperatures and pressures but providing the same alcohol conversion.

4.1.4 Alcohol Concentration

The effect alcohol concentration has on the product distribution was investigated with Catapal B and Versal B at conditions of 330 °C, 150 psig, and a GHSV of 2500 sl/kg-hr (Figure 4.1.7). At alcohol concentrations of 5 mol%, both catalysts showed conversions of almost 100%. At 10 mol% isobutanol, the difference in catalyst activity becomes more apparent. The decrease in conversion for Versal B was 3.8% for a 5% increase in alcohol concentration while that for Catapal B was only 2.1%. Catapal B demonstrated the same activity at 15% alcohol feed as did Versal B at 10%. These results indicate that a significantly lower space velocity will have to be used to obtain high conversions (>90%) when the concentration of isobutanol is raised to near 100%. Isobutene yields demonstrate the same trend as was established earlier. As the alcohol conversion decreases from 100 to 90%, the isobutene yield increases toward a maximum.

4.1.5 Comparison of the Alumina Dehydration Catalysts

In summary, several catalysts were investigated for use in a slurry reactor for the intramolecular dehydration of isobutanol to isobutene. The goal is to achieve high conversion of the alcohol while maintaining a high selectivity to the branched olefin for use as a feed stock for MTBE production. High overall productivity is essential to be economically competitive with the two stage process involving isomerization of n-butane.

In evaluating the catalysts performance, both activity and selectivity are critical to the viability of the process. Analysis of the experimental data in the process variable section had shown that a relationship existed between the isobutanol conversion and isobutene selectivity. Figures 4.1.8 and 4.1.9 illustrate this relationship for the four catalysts. The data are for a range of temperatures, pressures, GHSV, and isobutanol feed concentrations to show that the trend is process variable independent. The selectivity of isobutene, linear butenes, and diisobutyl ether are a function of isobutanol conversion and variations in the process variables producing the same conversion also produce the same product distribution. This conclusion is true for conversions greater than 30-40%. Below this the yield of isobutene and diisobutyl ether are more dependent on the process variables. This appears to be due to the much higher concentrations of ether at these conversions. Limited data available at these low conversions makes it difficult to offer a conclusion on this phenomena.

All of the catalysts demonstrate an isobutene yield (based on the isobutanol converted) of 0.90 or better at conversions of 60-70% and higher. From 75 to 98% conversion, the four catalysts all provide yields ranging from 0.92 to 0.94 with the maximum occurring at about 90% conversion. Therefore, all four catalysts are capable of obtaining high yields of isobutene. The key difference is that different operating conditions are required by the different catalyst to obtain these high yields. A better measure of the performance is illustrated in Figure 4.1.10 where the yield of isobutene, based on isobutanol feed, is plotted. This data accounts for both the conversion and the product selectivities. Catalyst Al-3996R demonstrates the best performance followed by Catapal B in the range of operating temperatures at LaPorte, namely 290-310 °C. At 330 °C there is no difference between the catalysts.

These results show that Al-3996R is a viable catalyst for slurry-phase dehydration of isobutanol and is recommended for a trial at the AFDU. Further testing of the catalyst before the trial should include high concentrations of isobutanol and long-term life tests. The data points for Versal B at 44 and 48% conversion represent replicates of the same operating conditions at the start and end of the test series. This variation may indicate that a significant change in catalyst performance occurs over time. No data is available on catalyst performance for longer than eight hours of continuous alcohol feed. The alcohol feed was stopped overnight while a small purge of nitrogen was maintained.

4.2 Controlling Isobutene Yields

The primary product in the dehydration of isobutanol is isobutene. Production of diisobutyl ether and linear butenes represents a yield loss based on the production of MTBE. Therefore, it is of interest to investigate ways to alter the catalyst selectivity to decrease the production of these other compounds. Since running the reaction at conditions which produce high conversion of alcohol also reduces the production of ether to zero, the study has focused on decreasing the isomerization of the isobutene to linear butenes.

4.2.1 Catalyst Impurities

In the literature many authors have shown that the activity of aluminas depends on their method of preparation.[14,15,16] According to the findings of Pines and Haag[16], aluminas containing no alkali contain a substantial number of strong acid sites; whereas, aluminas prepared from alkali aluminates contain a large number of weak acid sites. If this variation in acid site strength is the result of incorporated alkali in the alumina structure, then a high alkali content should lead to a higher isobutene selectivity. It is believed that isomerization of the branched structure occurs on these strong acid sites. The levels of sodium in the catalysts are listed in Table 4.2.1 as weight percent Na_2O. Isobutene yields (based on converted alcohol) are also listed in Table 4.2.1 for two different space velocities at conversions of 95% and better. While the highest sodium content alumina (Versal B) has the highest yield at both space velocities, the yields of the other three catalysts do not agree with the order of their sodium levels. Therefore, the results do not indicate any functionality of the isobutene selectivity on the sodium level for sodium levels covering two orders of magnitude.

In addition, variations in the catalyst activity do not coincide with the levels of sodium. This sodium is present in the alumina as an impurity. Other impurities include silicon, iron, carbon, and sulfur. Because the level of sodium in these catalysts represents a good correlation to the total level of impurities, this means that the activities are not related to the purity level of the catalyst. It is believed that the variation in the catalyst activity is due to differences in the catalyst surface areas and pore volumes after calcination. This is being investigated through characterization of the physical properties of the catalysts both before and after calcination.

4.2.2 Catalyst Doping for Enhanced Isobutene Selectivity

The literature indicates that the surface of alumina contains acidic and basic sites. These acid sites consist of both Lewis and Bronsted type of varying strength. It is believed that rearrangement of the branched alkene occurs by re-adsorption of the newly formed molecule onto a strong acid site as opposed to rearrangement via a carbonium ion during the primary reaction. According to the literature, it is possible to alter the distribution of acid site strengths by doping the alumina with an alkali metal.[17] In this manner, the number of strong acid sites is decreased and consequently a higher selectivity to the branched alkene produced. Attempts were made to alter the selectivity distribution of the butene isomers by doping two aluminas (Catapal B and Versal B) with potassium obtained from potassium hydroxide. The weight loading of potassium ranged from 0.2 to 0.8 wt.%. The catalyst doping was carried out using the spray method after which the catalyst samples were calcined at 500 °C.

The results from experiments performed at 330 °C, 150 psig, and 5 mol% isobutanol are presented in Figure 4.2.1 for Catapal B and Figure 4.2.2 for Versal B at GHSVs of 2500 and 6000 sl/kg-hr. For Catapal B there is a dramatic decline in catalyst activity with increased potassium loading. At 2500 sl/kg-hr the isobutanol conversion decreased 6.0, 14.4, and 31.8% as the potassium weight percent was increased to 0.2, 0.5 and 0.8%. For a GHSV of 6000 sl/kg-hr the isobutanol conversion dropped 13.8, 30.7, and 53.2% for the same potassium loadings. This large decline in activity with the increase in space velocity was seen before with the four aluminas. Again when the operating conditions are varied so as to cause a decrease in isobutanol conversion, the gap in performance between catalysts increased. Isobutene yields follow the same trend established for the four aluminas. When the conversion was greater than 90%, a decline in conversion toward 90% resulted in an increase in isobutene yield while a decrease in conversion below 90% caused a significant drop in the yield.

Versal B demonstrated only a 0.6 and 2.5% decline in conversion on going to a 0.2 wt.% potassium loading at 2500 and 6000 sl/kg-hr, respectively. This was a much smaller change than was observed for the Catapal B series. This difference may be the result of an inaccurate measure of the weight loading for Versal B since the pore volume had to be estimated. Since the conversions for Versal B are all relatively the same, the isobutene yields can be compared directly. At both space velocities, the 0.2 wt.% K doped catalyst demonstrated a sizable increase in yield over that of the base alumina. This suggests that an increase in the weight loading of potassium causes a decrease in skeletal rearrangement of the branched structure. However, the decline in activity offsets this increase somewhat providing only about a 1% improvement in overall yield based on total isobutanol feed.

A direct comparison of the isobutene yields for the doped Catapal B series is impossible using Figure 4.2.1 because of the large variation in activity. To properly compare the catalysts in terms of yield performance, the isobutene yield was plotted as a function of conversion for experiments conducted at 330 °C (Figure 4.2.3). While the curves do not all overlap, a comparison can be made at 90% conversion by extrapolating the Catapal B curve slightly following the established curvature. From this it is evident that doping the alumina with potassium does provide an increase in the isobutene yield as was seen with the Versal B. An increase in yield can be obtained with an increase in potassium loading up to about 0.5 wt.%. Potassium weight loadings higher than this do not provide any benefit and in fact are detrimental with regard to conversion. The problem is that the increase in isobutene yield is more than offset by the decline in catalyst activity. As an example of this, Table 4.2.2 lists the range of operating conditions that must be used to obtain the same conversion among the doped catalysts in order to take advantage of the increased yield. Obviously using a doped alumina decreases the economic viability of the process.

4.2.3 Effect of Feed Composition on the Product Spectrum

Commercial application of the liquid phase technology for the production of isobutene will consist of two stages: 1. production of isobutanol from coal or natural gas derived synthesis gas, and 2. dehydration of the isobutanol to isobutene. The product isobutene can then be used for the production of methyl tertiary-butyl ether. Tertiary ethers of higher carbon number also have high octane numbers and can be used in transportation fuels. Current isobutanol synthesis work has demonstrated a high selectivity for 2-methyl-1-alcohols as well as isobutanol. An alcohol feed consisting of the approximate higher alcohol composition from isobutanol synthesis was used for two dehydration experiments. The composition of the alcohol mixture is listed in Table 4.2.3. The two experiments were performed at 330 °C, 150 psig, and GHSV of 2500 and 1050 sl/kg-hr. A 0.8 wt.% K doped Catapal B catalyst was used. The feed consisted of about 5 mol% mixed alcohol in nitrogen.

Table 4.2.3 lists the molar selectivities of the individual branched alcohols in the feed along with those of the corresponding olefin products. These selectivities represent the ratio of branched to total alcohol for the feed and branched to total alkenes in the product stream. Also listed is the selectivity of the grouped 2-methyl-1-alkenes compared to that of the branched alcohols in the feed. All of the branched alcohols exhibited isomerization, but the degree of isomerization increased with increasing carbon number. The selectivity of isobutene to the total butenes is higher than expected based on experiments using a pure isobutanol feed. The selectivity of isobutanol to C4 alcohols in the feed was 89.2%. That of isobutene to C4 alkenes was 87.0% for the high space velocity experiment. For a pure isobutanol feed, the selectivity for isobutene at approximately the same conversion was about 96.2%. Accordingly, if the isobutanol underwent the same degree of isomerization in the mixed alcohol feed as when used by itself, the selectivity of isobutene should be 85.8%. This difference in isomerization selectivity indicates that the presence of the higher carbon number alcohols hinders the isomerization of the isobutanol. This result is consistent with those of Fran Waller (CSTC) who performed dehydration experiments in a packed bed reactor. Fran observed a difference of about 2% compared to the difference of 1.2% listed here. This difference is believed to be outside experimental error.

The second experiment showed this isomerization effect more clearly. This experiment was performed at a GHSV of 1050 sl/kg-hr providing a longer residence time for the alcohol feed. The selectivity of isobutene to total butenes (87.5%) was slightly higher than that for the high space velocity experiment. At this higher conversion, the selectivity for a pure isobutanol feed was 96.0%. The expected isobutene isomerization selectivity for the mixed feed was 85.6%. Therefore, this experiment shows an even larger difference between the observed and expected selectivities.

In the second experiment, significantly lower selectivities for the C5 and C6 branched olefins were observed. The decrease of the C5 and C6 branched olefin selectivities with the increased alcohol conversion is consistent with the trend observed in the pure isobutanol experiments. The C4 selectivity does not follow this trend but remains approximately constant with an increase in conversion. The reason for this is not clear.

Feeley et al.[18] tested the use of a gamma alumina catalyst for the direct synthesis of methyl tertiary-butyl ether from a mixed feed of isobutanol and methanol. While this effort failed, he found that at 250 °C the only butene formed from dehydration of the isobutanol was isobutene. This suggested the possibility that methanol may also hinder isomerization of isobutanol. In the synthesis of isobutanol, an equilibrium concentration of methanol is also formed making it feasible to feed a mixture of isobutanol and methanol directly to the dehydration reactor. A dehydration experiment was performed using a liquid feed consisting of a 2:1 molar ratio of isobutanol:methanol. Conditions for the experiment were 330 °C, 33 psig, 6 mol% alcohol in nitrogen, and GHSV of 1600 sl/kg-hr using a 0.5 wt.% K doped Catapal B catalyst. A higher temperature was used because the conversion at 250 °C is too low to make the process economical. Table 4.2.4 shows that the same degree of isobutanol conversion is obtained for both feeds; however, the isobutene yield for the pure feed is significantly higher. The mixed feed produced methylisobutyl ether resulting in the yield loss. The yield ratio of isobutene to linear butenes is 19.27 for the pure isobutanol feed and 20.00 for the mixed feed. This indicates that there may be a slight decrease in the isomerization of the branched structure with the methanol co-feed, but the loss in yield makes this an undesirable process.

An interesting result from the methanol/isobutanol experiment is that significant amounts of dimethyl and methylisobutyl ether were formed (about 10 and 7 wt.% of the organic products) while only a trace amount of diisobutyl ether was formed (about 0.2 wt.%). When the higher alcohols mixture was used, no compounds with higher molecular weights than diisobutyl ether were detected on the GC indicating that either higher carbon number ethers are unstable or the mechanism for their formation is unstable at this temperature. These results are consistent with the findings of Knozinger and Kohne[13] in which ethers of lower carbon number were stable up to higher temperatures over alumina.

4.3 Development of Kinetics for the Dehydration of Isobutanol

4.3.1 Mass Transfer or Kinetic Limitations

In determining a kinetic expression for the dehydration reaction it is important to separate mass transfer and kinetic effects. To accomplish this, a series of experiments were performed in which the impeller speed was varied to determine the rate at which the reaction becomes mass transfer limited. The experiments were performed at aggressive conditions of 310 °C, 500 psig, and GHSV of 11500 sl/kg-hr using catalyst Al-3996R gamma alumina. These conditions were used to obtain reaction rates significantly higher than those previously obtained. The feed consisted of 5 mol% isobutanol in nitrogen. The results of these runs are listed in Table 4.3.1. The reaction rate is the same for impeller speeds of 1200 and 2000 RPM. As the speed was lowered below 1200, the reaction rate decreased indicating mass transfer effects became important. All previous catalyst runs were carried out at an impeller speed of 1200 RPM and reaction rates were lower than those obtained in this set of experiments. Therefore, mass transfer effects can be neglected in analysis of the data.

4.3.2 Effect of Water on the Dehydration of Isobutanol

During the dehydration of isobutanol, one mole of alcohol reacts to form one mole of olefin and one mole of water. Therefore, water and isobutene are perfectly correlated. To develop a kinetic expression for this reaction, it is critical to separate the effects of water and isobutene. This was done by using two different feed compositions (3 moles isobutanol:1 mole water, 3 moles isobutanol: 2 moles water) to measure the effect water has on the reaction. Table 4.3.2 summarizes the performance of Al-3996R gamma alumina as a function of the feed composition for two different temperatures, 290 and 310 °C. The liquid feed rates were adjusted to give a reactor inlet composition of approximately 5 mol% isobutanol for all experiments. An increase in the concentration of water in the feed caused a decrease in isobutanol conversion. The reaction rate is a strong inverse function of the concentration of water present in the reactor. This is consistent with the findings discussed in the literature review section where water was found to inhibit dehydration.

4.3.3 Development of a Power Law Rate Expression

The conversion of isobutanol and the selectivity of isobutene obtained in these experiments is high. This might lead one to believe that development of a mechanistic expression for the dehydration of isobutanol is straight forward. However this is not the case. Figures 4.1.8, 4.1.9, and 4.2.3 show the functionality between the isobutanol conversion and the isobutene yield (based on converted isobutanol). As was discussed earlier, the yield of isobutene decreases as the conversion increases toward 100%. At conversions greater than 98%, there is a rapid decline in the isobutene yield. Several possibilities exist for the mechanism of linear butene formation as has been discussed earlier in this text, none of which have been verified. These possibilities include re-adsorption of the isobutene and subsequent isomerization, isomerization of the branched structure during the primary dehydration step, decomposition of the ether, or even a combination of these.

The uncertainties in the mechanism of the reaction make it difficult to derive a mechanistic rate expression. However, this does not mean that a meaningful correlation of the data cannot be obtained. An empirical power law rate expression was used to correlate the experimental data. The parameters for this expression were determined using the fugacities of the products in the reactor exit stream. The concentrations of the butenes were lumped together to get a rate which predicted the formation of butenes and not necessarily just isobutene. Since the yield of isobutene is at least 90% and greater for most of the experiments, this rate expression basically predicts the formation of isobutene. Small traces of propene, butane, and isobutane were detected in most of the runs. These concentrations were never more than a fraction of a weight percent and so were neglected in developing the rate expression.

A regression was performed on the data neglecting the concentration of ether since it represents only a small percentage of the product stream for most of the runs. The expression for the rate is shown below.

$$-r_{iBuOH} = k\, f_a^{0.81}\, f_o^{0.56} / f_w^{2.32}$$

activation energy= 44247 cal/gmol
correlation coefficient=0.93
fa, fo, and fw are the isobutanol, butene, and water fugacities

The fit to the data is illustrated in Figure 4.3.1. The correlation between the rate expression and the experimental data is quite good.

Since the concentration of diisobutyl ether increases to about 10 wt.% of the products as the conversion decreases from 100 to 50%, a second regression was performed to test the significance of the ether. Here the ether in the product stream was taken to be unreacted alcohol thereby accounting for all of the products. The results for this regression are listed below.

ether assumed unreacted alcohol $-r_{iBuOH} = k\, f_a^{0.79}\, f_o^{0.57} / f_w^{2.35}$

activation energy= 44660 cal/gmol
correlation coefficient=0.92
where fa, fo, and fw are the isobutanol, butene, and water fugacities

An identical correlation is obtained when the ether is assumed to be unreacted alcohol. While this rate expression does not provide a mechanistic explanation for the dehydration reaction, it does provide a starting point for developing a mechanistic expression. Further work is needed to understand the significance of the ether formation and the isomerization of isobutene before a truly accurate rate expression for the formation of isobutene can be developed.

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