Appendix I: Literature Survey

Memorandum

To:	T.H. Hsiung	Dept./Loc.:	PG&E Research/Iron Run
From:	B. E. Latshaw	Dept./Ext.:	PG&E Research/3995
Date:	24 March 1992		

Subject: Literature Report and Related Information - Dehydration of Isobutanol to Isobutylene

---

cc: D. M. Brown
T. W. Copeman
D. M. Herron
R. P. Underwood
F. J. Waller

SUMMARY:

A thorough literature search was performed to obtain information on the dehydration of isobutanol to isobutylene. Because of the limited information available on this particular reaction, the search strategy was broadened to the dehydration of alcohols to alkenes with special interest in obtaining information on the catalyst, reactor type, and reaction conditions used in the work. Work on the dehydration of ethanol was not included because of the lack of correlation between the mechanisms followed for the dehydration of ethanol and isobutanol, i.e. isomerization is an important factor for isobutanol.

A number of catalysts have been used in the literature to study the dehydration of alcohols to alkenes. These catalysts can be divided into four groups: aluminas and modified aluminas, zeolites, metal phosphates and sulfates, and oxides. Alumina has been the most widely used dehydration catalyst and has been implemented into at least two pilot plant operations for the dehydration of isoamyl alcohol. From this information, it appears that the catalysts best suited for the dehydration of isobutanol would be a treated alumina or possibly just a less pure gamma-alumina, a phosphate or sulfate modified zirconia, or a calcium phosphate. These catalysts were specified because of their inactivity for producing the butanol isomers during the course of the reaction. The reaction conditions obtained from the literature indicate temperatures ranging from about 300 to 400 C and pressures around atmospheric. The thermodynamic calculations for the dehydration of isobutanol show that the reaction is endothermic and therefore, requires the higher temperatures in order to obtain a reasonable conversion. According to the literature, the majority of the work has been performed in packed bed reactors; however, a limited amount of literature has been found which describes a process for the dehydration of tertiary-butyl alcohol utilizing a slurry phase reactor. Attempts are being made to obtain more information on this matter. It was difficult to make any reasonable conclusions in regard to the catalyst life expectancy. It appears that the occurrence of side reactions which lead to carbon formation on the catalyst surface should be inhibited by the absence of strong acid sites.

INTRODUCTION:

The dehydration of isobutyl alcohol to isobutene is an important reaction because of the use of isobutene as a feed stock for the production of methyl tertiary butyl ether (MTBE). Since it has been shown that isobutyl alcohol can be successfully produced from coal derived syngas, the next step to the production of MTBE is to develop the dehydration process of isobutanol. A literature review of the dehydration of isobutyl alcohol has been conducted; however, there does not appear to be a large amount of information on this specific reaction. In regard to this fact, an expanded view of the literature was undertaken to obtain any available information on the dehydration of alcohols with a similar carbon structure, i.e. 2-methyl-1-alkanols. The desired product of the dehydration reaction is isobutene (2-methyl-1-olefin), but it is quite possible to obtain all of the butene isomers. Thus, a catalyst and reaction conditions need to be determined which will give isobutene as the primary product and inhibit to a large extent any isomerization from occurring.

DEHYDRATION REACTION:

Since the dehydration mechanism is undoubtedly a function of both the structure of the catalyst as well as the structure of the alcohol, a single reaction mechanism cannot be established. According to the literature though, alumina appears to have been the most widely used dehydration catalyst and therefore, the most widely studied. In order to obtain some insight into the reaction mechanism, information will be presented on the dehydration of alcohols over alumina with specific reference to isobutanol when applicable.

In general, dehydration of alcohols occurs over an acid catalyst. On alumina, two different acid sites are present, namely Lewis and Bronsted. The Bronsted acid sites result from the surface hydroxyl groups and are considered on average to be weakly acidic.[1] The Lewis acid sites result from the incomplete coordination of surface aluminum atoms by surrounding oxygen atoms.[2] These incompletely coordinated aluminum atoms arise due to removal of the surface hydroxyl groups through condensation with adjacent hydroxyl groups and evolution of water. This removal of surface water also creates Lewis base sites which are oxygen ions.[2]

The adsorption of the alcohol to the surface occurs through hydrogen bonds between the alcohol hydroxyl group and the surface hydroxyl group and oxide ion.[3] At this point it is believed that the reaction scheme is slightly different depending on the structure of the alcohol.[3] The schemes proposed are based on the fact that the alumina contains only weak to moderate acidic sites and thus the reaction can be compared to dehydration in dilute aqueous acids. Taft et al.[4] found that tertiary alcohols abstract the hydrogen from the acid forming a carbonium ion basically free of covalently bonded water. Less stable secondary carbonium ions were found to be stabilized by specific interaction with two water molecules indicating a more concerted mechanistic character.[5] Dostrovsky and Klein[6] determined that oxygen exchange with primary alcohols in dilute acid solution occurred through a concerted mechanism and not by way of a carbonium ion.

The mechanism of dehydration for a primary alcohol such as isobutanol occurs through abstraction of the β-hydrogen of the alcohol by the surface oxide ion with subsequent cleavage of the alcohol hydroxyl group forming water and a surface oxide ion.[7] This mechanism has been concluded through a number of experimental observations. Knozinger[8] found that if aluminum hydroxide (which exposes solely hydroxyl groups at the surface) is used as the catalyst, there is complete inactivity for the dehydration of tertiary butanol. However, if the catalyst is heated such that the trihydroxide losses water to form the monohydroxide resulting as well in the formation of oxygen and aluminum ions, the dehydration reaction is observed. This indicates that other surface sites must take part in the formation of olefins. It has also been shown that selective poisoning of the Lewis acid sites by pyridine does not significantly alter the dehydration of alcohols.[8] Roca et al.[9] on the other hand have verified the participation of basic sites by poisoning experiments with tetracyanoethylene.

The rate limiting step during the dehydration reaction has been studied by Knozinger and Scheglila.[10] By examining primary kinetic isotope effects for the dehydration of tertiary, secondary, and iso-butanol in the gas phase, they determined that deuteration of the hydroxyl group does not cause an isotope effect and thus excludes the hydroxyl proton from any rate determining participation. This result also excludes the desorption of water as being rate determining at least in the case where the water is adsorbed by hydrogen bonds to hydroxyl or deuteroxyl surface groups. The kinetic isotope effect for β-carbon deuteration was greatest for the primary isobutanol and least for tertiary butanol. At temperatures below 200 C, they believe that all three alcohols exhibit E 2-like behavior, but as the temperature is raised the mechanism for tertiary alcohol shifts to E 1-like. An E2 reaction mechanism involves a single transition state in which the base pulls a proton away from the carbon while the hydroxide ion simultaneously departs allowing the double bond to form. The E1 reaction mechanism however, involves two steps whereby the alcohol undergoes cleavage of the hydroxyl ion with formation of a carbonium ion. This carbonium ion then loses a proton to the base to form the alkene. The results presented by Knozinger and Scheglila[10] reaffirm the mechanisms postulated earlier by Pines and Manassen[3] for the dehydration of tertiary, secondary, and primary alcohols on weak acid sites.

The mechanism for dehydration is not the same for all alcohols. Arai et al.[11] found while studying the dehydration of ethanol that at low temperatures ($T<135$ C) the major product desorbed from the alumina catalyst was diethyl ether. At higher temperatures they found a decrease in ether formation and an increase in ethylene formation. They postulated that the ether was formed by reaction of two nearby surface ethoxides. The presence of the surface ethoxides was verfied through IR studies. Knozinger and Kohne[12] however, found ethylene to be produced only above 250 C during ethanol dehydration. They believed that the ethylene was formed directly from dehydration as well as through decomposition of the ether. As the temperature was increased, the ether composition decreased significantly. The difference between the two findings is most likely a result of slight variations in the catalyst as well as the fact that Knozinger and Kohne performed continuous operation while Arai et al. performed batch experiments. Knozinger and Kohne proposed that the ether formed by reaction of an adsorbed alcohol with a surface ethoxide. They found a similar behavior for straight-chained alcohols up to n-hexanol; however, the temperature range in which ether could be isolated as the only product decreased with increasing chain length. They were also unable to detect any ether as a dehydration product of the branched butanols. This appears to be due to the instability of the alkoxide of the branched butanols. Surface alkoxides were detected by IR spectroscopy for the ether-forming alcohols whereas no surface alkoxide could be detected for the olefin-forming alcohols.[2] Thus it appears that the dehydration of isobutanol over alumina occurs through the concerted mechanism proposed by Pines and Haag.[7]

The E 2-like mechanism for dehydration of primary and secondary alcohols has been fairly well accepted. It is the transition state during the dehydration of the alcohol which appears to still be in question. Pillai and Pines[13] as well as Kibby et al.[14] had determined that alcohol dehydration on γ-alumina occurs as the trans-elimination of the elements of water. It has also been found that when formation of the cis- and trans- isomers is possible, the cis-olefin forms preferentially.[2,3,7] From the results of selectivity studies, Schwab and Schwab-Agallidis[15] proposed that the dehydration proceeded in pores and crevices of the catalyst. This view was also taken by Pines and Manassen[3] and Pines and Pillai[16] on the assumption that acidic and basic sites would be located on opposite sides of the pore. This scheme would indicate a reaction controlled by diffusion which has never been observed for alumina. Knozinger et al.[17] proposed that the alcohol molecule adsorbed onto the surface exercises as a whole vibrational motions, such that the $O\text{-}C_{\alpha}\text{-}C_{\beta}\text{-}H$ plane inclines to the surface. This would lead to the sterically more favorable conformation where bulky substituents are farthest away from the surface leading to preferential cis formation. Sedlacek and Kraus[18] have determined from quantum chemical modelling using the adsorbed state proposed by Knozinger et al.[17] that anti-elimination is the more energetically favorable path on the alumina surface. Sedlacek[19] was also able to explain the significant preference for cis-olefin formation by taking into account geometric and electronic factors.

It appears that an E2 reaction mechanism is followed for the dehydration of isobutanol on alumina. According to Pines and Haag[7] as well as Knozinger and Scheglila[10], it appears that pure β-H elimination occurs to form the primary dehydration product. This olefin product may then readsorb onto the strong acid sites where it may undergo isomerization. It is also assumed that oligermization occurs on these strong acid sites when the olefin is readsorbed. This most likely can be avoided by either running at lower conversions so as to avoid the olefin concentration from building up to a point where the probability of readsorption becomes high or by selectively poisoning the strong acid sites. Running at lower conversions was proposed due to the observed increase in isomer composition with increased contact time. It is also possible that at higher temperatures (T>300 C) γ-H elimination may occur with sebsequent migration of the hydrogen or methyl group forming a number of isomers.[20]

DEHYDRATION CATALYSTS AND REACTION CONDITIONS:

The information presented in this section has been divided into subsections according to the type of catalyst used for the dehydration reaction, namely: aluminas, zeolites, metal phosphates and sulfates, and oxides. According to the literature, alumina is a widely used catalyst for the dehydration of alcohols. Because of this, the information regarding alumina has been organized according to the structure of the alcohol (mixed alcohols, 2-methyl-1-alkanols, and isoamyl alcohol) used in the reaction so as to provide only that information which is most relavent in regard to the dehydration of isobutanol. The type of reactor and reaction conditions used by the various authors is also discussed as well as any pertinent information with respect to catalyst fouling and competitive side reactions.

A. ALUMINA:

The surface of alumina contains both acidic and basic sites. These acidic sites range in strength from strong to weak. Pines and Pillai[21] found that by modifying alumina with ammonia it was possible to produce relatively pure primary β-H dehydration products from a number of alcohols such as 3,3-dimethyl-1-butanol without significant quantities of their isomers. Pines and Haag[7] found that by incorporating small amounts of sodium (0.001% - 1.5% weight) into the alumina, the activity for dehydration decreased as the sodium content increased, however the more significant finding was that the activity for isomerization decreased substantially. According to the findings of Pines and Haag,[22] aluminas without alkali contain a substantial number of strong acid sites; aluminas prepared from alkali aluminates contain a large number of weak acid sites; and aluminas impregnated with alkali-base contain a reduced number of acidic sites without an appreciable change in the strength distribution. When the alumina is impregnated with alkali base, it is quite possible that if the base concentration is low and the solute is nonselectively adsorbed, the solution may be depleted of solute before the pores are filled. This would lead to the nonpreferential decrease in acid sites. The fact that both isomerization and dehydration decrease on impregnation of an alkali-base could result from adsorption of the base on the aluminum ions as well as sodium exchange with the surface hydroxyl protons.

1. MIXED ALCOHOLS:

Several patents have been issued which describe the use of an alumina catalyst for dehydration of alcohols. Hofstadt et al.[23] suggested using an alumina catalyst impregnated with LiOH, KOH, or NaOH with alkali metal concentrations of 0.1 to 1.5 wt.%. for the dehydration of C_4-C_6 alcohols produced from a synthesis gas. An undisclosed alumina catalyst was proposed by Reichl[24] for the dehydration of a mixed alcohol stream produced from synthesis gas. Reichle[25] used a high-purity (alkoxide derived) γ-alumina with low impurity levels impregnated with metal nitrates for the dehydration of normal alcohols to high-purity α-olefins. The metal ion consisted of Ba, K, Rb, or Cs with a concentration on the doped catalyst of 0.05-2.0 wt.%. Reichle suggests a low impurity alumina most likely so that the poisoning can be controlled solely through impregnation with the metal nitrates. Alvila et al.[26] proposed the use of a commercially available (Harshaw) aluminum oxide catalyst for the dehydration of a stream of mixed butanols. The proportion of straight-chained: branched alcohols was 1.3:1. The preparation of α-olefins in high selectivity from fatty alcohols was described by Voeste and Buchold.[27] In their process, they used a γ-alumina doped with NH_3 to dehydrate the alcohols while inhibiting any isomerization. Min'ko and Timofeev[28] described a pilot facility which uses an aluminum oxide catalyst treated with 0.25% KOH for the dehydration of several normal alcohols and isoamyl alcohol. They found that using this catalyst they could produce 1-hexene with 90-95% selectivity.

The above mentioned dehydration reactions were carried out in packed bed reactors. The reaction conditions used were temperatures ranging from 300-500 C and pressures ranging from 0.5 to 1 atmosphere. The LHSV (liquid hourly space velocity) were on the order of 1-4 liters of alcohol feed per liter of catalyst per hour. These conditions were utilized to obtain a product stream which consisted of a high selectivity for the primary olefin.

2. ISOBUTANOL OR 2-METHYL-1-ALKANOLS:

The dehydration of isobutanol was performed by Kim et al.[29] using an aluminum oxide catalyst doped with 1.5-2% $Ca(H_2PO_4)_2$ to inhibit skeletal isomerization. The reaction was carried out at temperatures of 300-400 C and GHSV of 300-2500 providing contact times of 5 seconds or less. They found that the yield of isobutylene could be raised from 80% to 96% by modifying the alumina catalyst. It was determined by Kim et al.[30] that by carrying out the reaction in a fluidized bed reactor they were able to obtain results which were similar to those obtained in a fixed bed reactor.

Several patents were issued on the use of modified alumina as a dehydration catalyst for 2-methyl-1-alkanols whereby the modified alumina produces a higher yield of the 2-methyl-1-olefin. Specific increases in the product selectivity or yield were not always stated. Shioyama[31] proposed using a zinc aluminate catalyst which is prepared by mixing equimolar portions of γ-alumina and zinc oxide in a ball mixer and then processed to produce the final physical form. Results were obtained which were similar to those using a sodium modified alumina, but the zinc aluminate had a wider temperature range over which the maximum olefin yield was produced. He also determined that the zinc aluminate was more effective than simple mixtures of zinc oxide and alumina. Resofszki et al.[32] studied the dehydration reaction using a solid solution of iron oxide and aluminum oxide prepared by spray-decomposing the aqueous solution of the nitrates at 500 C. They found that the addition of 1-10 mole% of iron oxide caused a sharp decrease in the acidity of the catalyst as well as total inactivity for skeletal isomerization. A zinc aluminate catalyst was also suggested by John[33]. However, John used a γ-alumina which was impregnated with an aqueous zinc salt solution producing an alumina carrier with zinc aluminate on its surface. With this zinc aluminate he was able to obtain 1-pentene with better than 90% selectivity. Drake[34] proposed the use of an alumina treated by soaking it in a solution of an organic carboxylic acid and a diluent to produce 2-methyl-1-butene with a selectivity of 85-95%. The amount of carboxylic acid used in the treatment of the silica can range from about 0.01-0.1 g per gram of alumina. An alumina catalyst which was modified simply by heat treatment was utilized by Drake[35] for the dehydration of branched alcohols. According to his process, a mixed boehmite (aluminum oxide-hydroxide)/chi-alumina catalyst is heated to about 550 C for several hours under a stream of nitrogen. The result is a relatively pure chi-alumina which shows high selectivities for the primary dehydration products without subsequent isomerization.

The above discussed catalysts were utilized for the dehydration reaction of branched alcohols to their corresponding olefins. The reactions were carried out in fixed bed reactors over a temperature range of 250-450 C and pressures of 1-7 atmospheres. The alcohol was introduced to the reactor at a WHSV ranging from 0.1 to 20 grams of alcohol feed per gram of catalyst per hour along with an inert carrier gas flow of 40-50 liters per hour.

3. ISOAMYL ALCOHOL:

Two studies have been performed on the dehydration of 3-methyl-1-butanol to provide information for optimal pilot plant operation. The studies were concerned with determination of a catalyst and reaction conditions which would produce a product stream with a high yield of 3-methyl-1-butene and low concentrations of product isomers. Drake et al.[36] of the Phillips Petroleum Co. found that a base treated gamma alumina inhibited the formation of product isomers. The pilot plant utilized a packed bed reactor operating at about 300 C core temperature and a pressure of approximately 3 atmospheres. The alcohol feed was varied from 1.0-1.5 LHSV resulting in a product yield of greater than 85% 3-methyl-1-butene. It should be noted that the product yield dropped to about 70-75% when the unit was run on a lower purity feed. Nitrogen was used as a carrier gas for the alcohol feed. Early tests on the catalyst life revealed that approximately 1000 pounds of 3-methyl-1-butene were produced per pound of catalyst. The second pilot plant operation was described by Timofeev et al.[37] Their process relied on a γ-alumina impregnated with 0.25 wt.% KOH. The dehydration was carried out at approximately 380 C with an alcohol feed of 4 liters per liter of catalyst per hour. Under these conditions, they were able to obtain a product selectivity of about 70%.

B. ZEOLITES AND AMORPHOUS ALUMINOSILICA:

Several experimental studies have been carried out in which silica-alumina catalysts of various compositions have been used for the dehydration of isobutyl alcohol. Weisz and co-workers[38] looked at the molecular shape selective dehydration of the isomeric butanols on Ca-zeolites 5A and 10X. They found that approximately 100% conversion of the isobutanol could be obtained at 300 C on the 10X catalyst, but that negligible conversion occurred for the dehydration on the 5A. This implies that the isobutanol is excluded from the crystal interior of the zeolite 5A. Normal butanol was dehydrated to about the same extent on both. No analysis of the butene products was presented. Amorphous aluminosilica gels and zeolites having chemical compositions corresponding to that of type X zeolite were used for the dehydration of isobutanol by Levchuk and Dzis'ko.[39] Running the reaction at 310 C they determined that the conversion could be increased by lowering the space velocity; however, they also found a corresponding increase in the concentration of polymeric products. Over the range of space velocities used, normal butene isomers constituted approximately 20-30% of the product stream. Samples with low sodium content were found to decrease in activity quite rapidly with time. This could result from oligomer formation within the pores and their inability to diffuse out. Their results showed that at low conversions the rate of dehydration as well as isomerization were independent of the alcohol conversion, but both became dependent with increasing conversion. They also found a linear decay of both rates with increasing sodium content.

Makarova et al.[40,41] performed limited experiments on the dehydration of isobutanol on H-ZSM-5. Their reaction conditions were 100-150 C, 1 atmosphere pressure, and low conversions (<10%) such that the reaction was zero order with respect to isobutanol. They did not provide an analysis of the product stream butene isomer composition. IR studies were performed to determine a possible reaction scheme. They believe that the reaction occurs through formation of a surface alkoxide which reacts with the alcohol to form a hydrogen bonded ether. This ether, restricted from diffusing out of the channel intersection, decomposes to form a butene and an alcohol molecule. Under conditions of higher conversion or interupted alcohol flow, they found a significant increase in oligomer formation. They postulate this to arise from interaction of the butene with the highly reactive alkoxide as the butene is diffusing through the pore.

C. METAL PHOSPHATES AND SULFATES:

Hofstadt et al.[23] suggested using either an aluminum phosphate or a calcium phosphate as the dehydration catalyst for a mixed alcohol stream. However, they stated that they preferred using an aluminum oxide or calcium phosphate, $Ca_3(PO_4)_2$, as the dehydration catalyst so that secondary reactions (condensation and polymerization) could be suppressed. A phosphorous rich hydroxyapatite catalyst $Ca_9(HPO_4)(PO_4)_5OH$ was investigated by Kibby et al.[14,42] for the dehydration reaction of several alcohols. They found that upon dehydration of isobutanol they were able to obtain about 90% isobutene with 10% normal butenes. The reaction was carried out at 300-400 C and low conversions such that the reaction was zero order with respect to the alcohol concentration. The calcium rich form of this catalyst, $Ca_{10}(PO_4)_6(OH)_2$ makes it a suitable catalyst for alcohol dehydrogenation. Brett et al.[43] states that the dehydration reaction is catalyzed by the acidic phosphate hydrogen. Clearfield and Thakur[44] studied the dehydration of cyclohexanol using a zirconium phosphate catalyst. They found the catalyst to be very selective toward the dehydration reaction with little activity for isomerization or dehydrogenation. The reaction was performed over a temperature range of 300-400 C and they determined that the dehydration data fit a first order rate equation. Clearfield and Thakur also proposed that the primary active sites are the monohydrogen phosphate protons with a possible secondary active site being of the Lewis acid type.

A sulfate modified zirconia catalyst was proposed by Klier et al.[45] as a possible catalyst for the dehydration of isobutanol. They found that when a mixture of isobutanol and methanol were charged to the reactor, the catalyst proved to be efficient and highly selective for the production of isobutene with methanol dehydration suppressed. However, no work has been done to study solely the dehydration reaction of isobutanol with this catalyst. Thorton and Gates[46] studied the dehydration of isobutyl alcohol using a poly(styrene-divinylbenzene) matrix containing sulfate groups as the catalyst. The reaction was performed at approximately 100 C giving a mixture of butene isomers and isobutane formation at low substrate partial pressures. The reaction was accompanied by about a 20% decrease in rate over tens of hours of operation resulting from a catalyst which became covered in a dark, sticky tar. The catalyst deactivation was not observed with either isopropyl or sec-butyl alcohols. According to Knozinger,[20] it is believed that the dehydration of alcohols on ion exchange resins occurs through oxonium or carbonium ion intermediates.

D. OXIDE CATALYSTS:

Schwab and Schwab-Agallidis[15] studied the dehydration of ethanol to ethylene on a number of oxide catalysts (ZnO, TiO_2, Cr_2O_3, γ-Al_2O_3, CeO_3, and ThO_2) and found that the product stream from the alumina and thoria catalysts consisted of better than 90% ethylene. Canesson and Blanchard[47] found that on dehydration of secondary alcohols over thoria a high selectivity was shown for the formation of the 1-alkene. They proposed that the reaction proceeds as a syn-elimination occurring by an E1cB pathway. A reaction occurring by an E1cB mechanism involves the loss of a proton from the alcohol to the base with formation of a negatively charged carbanion which then losses the hydroxide ion in a separate step to yield the alkene. Studying the possibility of γ-H eliminations from certain alcohols during the course of dehydration at 300-350 C, Siddhan and Narayanan[48] found that thoria showed very little propensity for γ-eliminations whereas the products obtained from alumina doped with sodium exhibited a significant contribution from γ-eliminations. It should also be noted that alumina exhibited a much higher activity for the dehydration of alcohols such as 3-methyl-1-pentanol than did thoria.

The dehydration of isobutanol was observed by Kotsarenko and Malysheva[49] using binary compounds of the type aM_mO_n $(1-a)SiO_2$, where M=Al, Ga, Zr, Be, and Y as catalysts. The reactions were carried out over the temperature range of 275-350 C using a circulation-flow method with a circulation rate of 800 liters per hour. They found that with increasing alcohol concentration, the order of the reaction changed from first to zero on all of the catalysts. The results of their experiments showed that isobutylene made up about 60-70 mole% of all the butylenes formed for all of the binary compounds. They also found that a gamma-alumina sample produced about 95% isobutylene. No indication as to the chemical composition of the alumina was given. Results for the isomerization of an isobutylene feed showed that alumina and the binary compounds of Be and Y were inactive for this reaction. From their results they concluded that the dehydration reaction of isobutanol on the binary oxides occurs through a carbonium ion mechanism leading to a high rate of normal olefins. Davis[50] looked at the dehydration of branched secondary and tertiary alcohols over aluminum and molybdenum oxide at temperatures of 180-275 C. For certain alcohols (i.e. 2,2-dimethyl-3-pentanol) it was found that molybdena produced a significant quantity of products which resulted from skeletal isomerization whereas the alumina did not. Davis postulated that the skeletal isomerization resulted from the dehydration step and not from a secondary reaction. The acidity and basicity of a number of metal oxides were investigated by Gervasini and Auroux.[51] The catalysts were tested for the decomposition of isopropanol to propene and acetone. While it is difficult to make any conclusions about the use of these catalysts for the dehydration of isobutanol, there are a few points that should be mentioned. They found that the oxides of Mo and W gave propene in the temperature range of 400-430 K while those of Al, Nb, Ta, Ti, and Zr were active in the temperature range of 430-490 K. This would indicate that MoO_3 and WO_3 possess stronger acid sites than the other oxides. However, it should be noted that MoO_3 and WO_3 also gave acetone, an undesired product in the dehydration reaction, at lower temperatures.

DEHYDRATION IN A SLURRY REACTOR:

Some work has been undertaken in the use of liquid phase reaction technology for the dehydration of tertiary butyl alcohol (TBA). A patent issued to Dockner and Krug[52] describes a process in which a feed of TBA and nitrogen are passed into a packed quartz tube filled with vacuum gas oil (boiling point 400 C) containing about 5% resin catalyst. The reaction is carried out at 205 C giving 97% yield isobutene. Abraham and Prescott[53] discuss the processes utilized by several companies for the dehydration of tertiary butanol to isobutene. According to the authors, Cities Service dissolves the TBA and a p-toluene sulfonic acid catalyst in a reaction medium of xylene. The isobutylene is removed as a gas and the water separates out and is removed continuously. Nippon, Asashi, and Maruzen use powdered resin catalysts in a stirred reactor for their processes. It must be noted that the patents referenced by Abraham and Prescott could not be located as cited in their article.

THERMODYNAMICS:

Calculations were made to determine the heat of reaction as well as the change in the Gibbs free energy upon dehydration of isobutanol to form isobutene and water. The heat of reaction at 298 C and 1 atmosphere is 8.16 kcal/mole and the Gibbs free energy change is -0.64 kcal/mole. The entropy change was determined to be 24.1 cal/mole K. The heat of reaction was also calculated at 300 C with its value being 8.75 kcal/mole. Thus, the reaction is endothermic and will require the process to be run at elevated temperatures in order to obtain good conversions. Klotz[54] performed some equilibrium calculations for the dehydration reaction and found that the equilibrium favors almost 100% conversion in the temperature range of 100-300 C and that it was only slightly shifted toward isobutanol at elevated pressures up to 52 atmospheres. The adiabatic temperature drop for the reaction was also determined by Klotz[55]. He found that at inlet conditions of 1 atmosphere and 200 C the temperature dropped to 77 C for 100% conversion while for an inlet temperature of 300 C the temperature dropped to 130 C. The temperature drop for the low inlet condition is controlled by the condensation of water in the reactor.

CONCLUSIONS:

From the information that has been gathered on the dehydration of alcohols, and in particular 2-methyl-1-alkanols, it appears that the catalysts best suited for the dehydration of isobutanol would be a treated alumina or possibly just a less pure gamma-alumina, a phosphate or sulfate modified zirconia, or a calcium phosphate. The literature indicates that the reaction should be run at temperatures ranging from about 300 to 400 C and at pressures around atmospheric. From the thermodynamics it is seen that the reaction is endothermic and requires the higher temperatures in order to obtain reasonable conversion of the isobutanol. According to the literature, the majority of the work has been performed in packed bed reactors; however, some of the TBA dehydration processes indicate that a slurry phase reactor should provide the proper conditions for an efficient and economic isobutanol dehydration process. It was difficult to make any reasonable conclusions in regard to the catalyst life expectancy. It appears that a catalyst which does not possess strong acid sites such that isomerizations do not occur should also inhibit other side reactions from occurring which lead to carbon formation on the catalyst surface.

B. E. Latshaw

REFERENCES:

1. E. P. Parry, J. Catal., 2, 371 (1963).
2. H. Knozinger, Angew. Chem. Intern. Ed., 7, 791 (1968).
3. H. Pines and J. Manassen, Advan. Catal., 16, 49 (1966).
4. R. W. Taft Jr., E. L. Purles, P. Riesz, and C. A. De Fazio, J. Am. Chem. Soc., 77, 1584 (1955).
5. Manassen, J., and F. S. Klien, Chem. Soc. (London) Spec. Publ., 14, 4203 (1960).
6. I. Dostrovsky and F. S. Klien, J. Chem. Soc., 4401 (1955).
7. H. Pines and W. O. Haag, J. Am. Chem. Soc., 83, 2847 (1961).

8. H. Knozinger, Angew. Chem., 80, 778 (1968).
9. F. Fiqueras Roca, L. de Mourges, and Y. Tranbouze, J. Catal., 14, 107 (1969).
10. H. Knozinger and A. Scheglila, J. Catal., 17, 252 (1970).
11. H. Arai, J. Take, Y. Saito, and Y Yoneda, J. Catal., 9, 146 (1967).
12. H. Knozinger and R. Kohne, J. Catal., 5, 264 (1966).
13. C. N. Pillai and H. Pines, J. Am. Chem. Soc., 83, 3274 (1961).
14. C. Kibby, S. Lande, and W. Hall, J. Am. Chem. Soc., 94, 214 (1972).
15. G. Schwab and E. Schwab-Agallidis, J. Am. Chem. Soc., 71, 1806 (1949).
16. H. Pines and C. N. Pillai, J. Am. Chem. Soc., 83, 3270 (1961).
17. H. Klnozinger, H. Buhl, and K. Kochloefl, J. Catal., 24, 57 (1972).
18. J. Sedlacek and M. Kraus, React. Kinet. Catal. Lett., 2, 57 (1975).
19. J. Sedlacek, J. Catal., 57, 208 (1979).
20. H. Knozinger, "The Dehydration of Alcohols" in "The Chemistry of the Hydroxyl Group," S. Patai, ed., Interscience Publishers, 1971.
21. H. Pines and C. Pillai, J. Am. Chem. Soc., 82, 2401 (1960).
22. H. Pines and W. Haag, J. Am. Chem. Soc., 82, 2471 (1960).
23. C. E. Hofstadt, M. Schneider, and K. Kochloefl, U.S. Pat. 4,398,050 (1983).
24. E. Reichl, U.S. Pat. 4,534,772 (1985).
25. W. Reichle, Res. Discl., 283, 717, Union Carbide Corp. (1987).
26. L. Alvila, T. Pakkanen, O. Krause, and M. Joutsimo, U.S. Pat. 4,777,320 (1988).
27. T. Voeste and H. Buchold, DE Pat. 3,915,493 (1990).
28. T. Min'ko and A. Timofeev, Khim. Prom-st. (Moscow), (10), 595 (1986).
29. S. Kim, H. Chang, J. Che, and J. Rim, Choson Minjujuui Inmin Konghwaguk Kwahagwon Tongbo, 26 (6), 303 (1978).
30. S. Kim, H. Chang, J. Je, C. Lin, Choson Minjujuui Inmin Konghwaguk Kwahagwon Tongbo, (6), 47 (1979).
31. T. Shioyama, U.S. Pat. 4,260, 845 (1981).
32. G. Resofszki, J. Juhasz, T. Kovacs, and B. Jover, Geterog. Katal., 5th, Pt.1, 273 (1983).
33. C. S. John, GB Pat. 2,181,070 (1987).
34. C. Drake, U.S. Pat. 4,602,119 (1986).
35. C. Drake, U.S. Pat. 4,529,827 (1985).
36. C. Drake, M. Martinovich, and S. Marwil, Chem. Eng. Prog., 81, 52 (1985).
37. A. Timofeev, L. Romanchenko, I. Pis'man, and T. Min'ko, Prom-st. Kauch., (6), 6 (1982).
38. P. B. Weisz, V. J. Frillette, R. W. Maatman, and E. B. Mower, J. Catal., 1, 307 (1962).
39. V. S. Levchuk and V. A. Dzis'ko, Kinet. Katal., 10 (6), 1289 (1969).
40. M. Makarova, C. Williams, V. Romannikov, K. I. Zamaraev, and J. M. Thomas, J. Chem. Soc. Faraday Trans., 86 (3), 581 (1990).
41. C. Williams, M. Makarova, L. Malysheva, E. Paukshtis, K. Zamaraev, and J. M. Thomas, J. Chem. Soc. Faraday trans., 86 (20), 3473 (1990).
42. C. L. Kibby and W. K. Hall, J. Catal., 29, 144 (1973).
43. J. A. S. Brett, L. G. Christner, and W. K. Hall, J. Am. Chem. Soc., 89, 5535 (1967).
44. A. Clearfield and D. S. Thakur, J. Catal., 65, 185 (1980).
45. K. Klier, R. G. Herman, M. A. Johansson, and O. C. Feeley, Div. Fuel Chem., ACS Spring Meeting, April, 1992.
46. P. Thornton and B. C. Gates, J. Catal., 34, 275 (1974).
47. P. Canesson and M. Blanchard, J. Catal. 42, 205 (1976).

48. S. Siddhan and K. Marayanan, J. Catal., 59, 405 (1979).
49. N. S. Kotsarenko and L. V. Malysheva, Kinet. Katal., 24, 877 (1983).
50. B. H. Davis, J. Catal., 79, 58 (1983).
51. A. Gervasini and A. Auroux, J. Catal., 131, 190 (1991).
52. T. Docker and H. Krug, DE Pat. 3,317,165 (1983).
53. O. C. Abraham and G. F. Prescott, Hydrocarbon Proc., Feb., 51 (1992).
54. H. Klotz, APCI memo, "Equilibrium Conversions for Isobutylene/Alcohol Reactions," 6 November (1991).
55. H. Klotz, APCI memo, "Isobutanol Heats of Reaction," 30 January (1992).