Temperature programmed desorption-FTIR investigation of C₁–C₅ primary alcohols adsorbed on γ-alumina

P.A. Clayborne, T.C. Nelson, T.C. DeVore*
Department of Chemistry MSC 7701, James Madison University, Harrisonburg, VA 22807, USA

Received 22 July 2003; received in revised form 30 July 2003; accepted 30 July 2003

Abstract

Temperature programmed desorption (TPD)-FTIR was used to investigate the products chemical reactions produced when methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol desorp from γ-alumina into vacuum at elevated temperatures. Methanol and dimethyl ether desorbed for methanol and the alcohol, the ether, and the 1-alkene desorbed from the C₂–C₅ alcohols clearly indicating that some chemical reactions had occurred before the compounds desorbed. The mass of ether produced per gram of alumina decreased and the mass of alkene produced per gram of alumina increased as the number of carbons in the alcohol increased. The activation energies for the production of the ether and the alkene were identical within experimental error for the C₂–C₅ alcohols. With the exception of the formation of dipropyl ether, the activation energies found for the desorption of the reaction products agreed with the activation energies reported from kinetic measurements for the C₁–C₃ alcohols. PM₃ calculations indicated that the preferred mode of bonding for undissociated methanol was the Lewis acid interaction between the oxygen in the methanol and the aluminum on the model surface. Bonding to neighboring Lewis acid-base sites had the lowest reaction enthalpy when the methanol dissociated into methoxy radicals and hydrogen atoms while adsorbed on the surface.

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Keywords: Alumina; Arrhenius parameters; C₁–C₅ primary alcohols; Kinetics; Temperature programmed desorption

1. Introduction

Although several investigations into the kinetics of the dehydration of alcohols over alumina have been reported, the mechanisms for the formation of the products have not been established with certainty [1,2]. The reaction temperature, the type of alcohol, the form of the catalyst, and the addition of atoms such as the alkali or alkaline earth metals affect the reaction rates and the amounts of the products produced [1–9]. Depending upon the conditions used, the reaction of ethanol or 1-propanol produced the ether, the alkene, or both. With the exception of 2-propanol, the dehydration of a secondary alcohol over alumina generally does not produce the ether [10,11]. While there is growing consensus that the kinetics of these reactions can be modeled using the Langmuir–Hinshelwood mechanism [1–4,10–17] and most researchers have concluded that there is more than one type of surface site, there is no clear consensus about the nature of these sites [1,2,18–30]. Lewis acid, Lewis base, Broensted acid, and paired acid–base sites have been proposed as the active sites for these reactions. The uncertainty in and the possible complexity of the active sites are illustrated by the mechanism using each of these possible sites presented by Shi and Davis [1].

Temperature programmed desorption (TPD) is a well-established technique for characterizing catalyst sites and TPD has been used to investigate alumina catalyzed alcohol dehydration [31–38]. Most of these have used methanol as the reactant alcohol. The most complete investigation to date is the study of the desorption of methanol from single crystal Al₂O₃(010) under high vacuum conditions by Nishimura et al. [38]. This single crystal alumina produced a distribution of adsorption sites. The multilayer desorption enthalpy (48 ± 2 kJ/mol) and site centered first order desorption enthalpy (76 kJ/mol) were in reasonable agreement with the adsorption enthalpy (47 kJ/mol) and the activation energy (98 kJ/mol) reported for the alumina catalyzed production of methyl ether by Lin and Wang [23]. Nishimura et al. [38] found only the desorption of methanol under their experimental conditions. However, Trokhimenets et al. reported that dimethyl ether also desorbed from methanol adsorbed on α-Al₂O₃ [31]. 1-Al₂O₃...
[32], or θ-Al₂O₃ [33] at temperatures of ∼475 K and that methane, carbon monoxide, and hydrogen desorbed at ∼675 K.

TPD-Fourier transform IR spectroscopy was used to investigate the TPD of C₁–C₅ primary alcohols adsorbed on γ-alumina prepared by heating boehmite in air. The XRD lines of the pyrolyzed boehmite were broad (see Fig. 1) indicating either that the γ-alumina was poorly crystallized or that the particles of the product were too small to give a good diffraction pattern. This data permitted a direct comparison of the products produced as several primary alcohols desorbed from the same surface. Since several chemical reactions occurred on the surface, this data provided additional information about the mechanism of these dehydration reactions offered insights on possible steric hindrance on the product distribution. Although less certain, these investigations may also offer insight into the contributions from the primary alcohol in the mechanism of oxidative dehydrogenations to form alkenes from alkanes. In addition, semi-empirical molecular orbital calculations (PM3 level) were used to investigate the interaction between a methanol molecule and a model alumina surface to provide additional insight into the nature of the bonding sites.

![Fig. 1. XRD observed for calcined boehmite.](image-url)
2. Experimental

The IR cell used for these investigations has been described in detail previously [39–41]. It was constructed by using O-ring connectors to attach KBr windows to two opposing arms of an MDC Corp. four-way cross stainless steel vacuum flange. One of the remaining arms was connected to the vacuum pump. The fourth arm was attached to a sample tube that was constructed by sealing one end of a 25 cm long piece of 9 mm o.d. glass tubing. The sample was heated using a furnace assembly made by wrapping nichrome wire around a 12 mm o.d. quartz tube. The temperature of the furnace was controlled using an Omega power supply and was measured with a chromel–alumel thermocouple connected to a Fluke digital thermometer. The uncertainty in each temperature measurement was \( \pm 3 \) K.

A Nicolet Magna 750 FTIR was used to monitor the evolved gases. This spectrometer was set to collect and store one spectrum every 2 s for reaction times up to 60 min. Spectra were collected from 400 to 4000 cm\(^{-1}\) with 4 cm\(^{-1}\) resolution and the Nicolet–Aldrich spectral library was used to help identify the evolved gases.

The \( \text{Al}_2\text{O}_3 \) was prepared by heating chromatography grade \( \text{Al}_2\text{O}_3 \) powder (Baker Analyzed Reagent) to 800 K in vacuum and then calcining this product in air over a Bunsen burner flame to red heat. X-ray diffraction indicated that the \( \text{Al}_2\text{O}_3 \) was boehmite prior to heating and was poorly crystalline/H\(_9\)25\(-\)alumina after heating (see Fig. 1). The surface area was determined by adsorbing liquid water or gaseous ammonia on the surface, monitoring the desorption in the TPD apparatus, and measuring the mass changes that occurred as the compound desorbed. The mass change was used to calculate the number of molecules covering the surface and the area covered by each molecule was determined from theoretical calculations. The results of this procedure for both water and ammonia adsorbed on the surface indicated that the surface area was \( 225 \pm 25 \text{ m}^2/\text{g} \). Most of this stated uncertainty comes from the uncertainty in the area occupied by each molecule.

Sufficient liquid alcohol (Fisher) to totally wet the sample was added to the freshly calcined \( \text{Al}_2\text{O}_3 \) powder. The excess alcohol was allowed to evaporate in air and the dried sample was stored in a closed desicator until used. Approximately 0.25 g of this solid was loaded into the sample cell and pumped under a dynamic vacuum until the pressure returned to the baseline value (~50 mtorr) immediately prior to use. The sample was then weighed to determine the mass of the alumina and the alcohol. Weighing the sample after it had been heated in the TPD apparatus gave the mass of the alumina that had been used. The difference in these masses gave the amount of alcohol that had been adsorbed.

The sample was heated at a constant rate (usually between 5 and 10 K/min) from 300 to 700 K. The FTIR monitored the composition of the evolved gases as the sample was heated and the IR intensities for characteristic IR bands of each molecule were used to determine the extent of reaction [40,41]. The kinetics of the reaction could then be determined from the extent of reaction following the procedure given by Brown [42] and by Spinicci [43]. Since the extent of reaction can be used with no additional corrections to determine the activation energies, these values are only limited by the uncertainty in each datum point. The standard error from the least squares procedure used to fit the data and the data reproducibility of duplicate sets of data indicate that the reported values are uncertain by less than \( \pm 10 \text{ kJ/mol} \). However, absolute measurements such as the percent composition of the evolved gases, the absolute reaction rates, or the Arrhenius frequency factors require that

![Fig. 2. IR spectra observed for the temperature programmed desorption of methanol from alumina.](image)
Fig. 3. The desorption profiles observed for the desorption of methanol, dimethyl ether, and the total intensity of all of the evolved gases from alumina. The sample was heated from 300 to 700 K at 7 K/min.

Fig. 4. The desorption profiles observed for the desorption of ethanol, diethyl ether, ethene and the total intensity of all of the evolved gases from alumina. The sample was heated from 300 to 700 K at 7 K/min.

3. Results and discussion

The TPD for methanol reported here for poorly crystalline γ-alumina agreed with the results for crystalline alumina reported by Trokhimets et al. [31–33]. IR bands that could be assigned to methanol and dimethyl ether were clearly identified (see Fig. 2) indicating that a chemical reaction had occurred during the desorption. The desorption profile for methanol indicated at least two types of bonding to the surface (see Fig. 3). The intensity of the first methanol peak varied with sample loading indicating that methanol was not strongly bound to this site. The dimethyl ether evolution

does not need to be corrected for differences in the molar extinction coefficients. Although absolute IR intensities calculated using theoretical measurements and IR intensities measured by flowing the pure compounds through the IR cell at a measured rate were used to make these corrections, the absolute reaction rates and the Arrhenius frequency factors could be in error by as much as a factor of 2. This error was estimated based upon the measured data scatter caused by the uncertainties in the calibrations and the difficulties in accurately separating blended bands in the spectra. The percent compositions are subject to the same constraints but they should be good to better than ±10%.
evolved concurrently with the second methanol peak and was between 30 and 40% of the desorbed gas for samples with complete monolayer coverage. The evolved gas curve for dimethyl ether was fit using second order kinetics following the procedure given previously by Brown [40–43]. The activation energy determined for this process (92 ± 10 kJ/mol) was consistent with the activation energy for the formation of dimethyl ether (98 kJ/mol) [23] reported previously from kinetic measurements. The complex shape of the methanol TPD curve is consistent with the previous reports of multiple adsorption sites [1,2,18–38]. No further analysis of it was done since careful analyses of it had been reported previously [38].

The TPD curves for ethanol, 1-propanol, 1-butanol, and 1-pentanol were qualitatively similar. Each showed the evolution of alcohol, the ether, and the 1-alkene (see Figs. 4–7) indicating that chemical reactions were occurring during the desorption processes. The alcohol TPD curves have complex shapes indicative of multiple adsorption sites, but the ether and 1-alkene have regular shapes and were analyzed assuming desorption from one site. The amount of loading affected the shape of the alcohol desorption curve. The intensity of the lowest temperature peak was most affected depended upon the amount of loading and its intensity decreased as the sample was pumped under vacuum. This effect is illustrated by comparing the TPD curve of ethanol evolved concurrently with the second methanol peak and was between 30 and 40% of the desorbed gas for samples with complete monolayer coverage. The evolved gas curve for dimethyl ether was fit using second order kinetics following the procedure given previously by Brown [40–43]. The activation energy determined for this process (92 ± 10 kJ/mol) was consistent with the activation energy for the formation of dimethyl ether (98 kJ/mol) [23] reported previously from kinetic measurements. The complex shape of the methanol TPD curve is consistent with the previous reports of multiple adsorption sites [1,2,18–38]. No further analysis of it was done since careful analyses of it had been reported previously [38].

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shown in Fig. 4 to the TPD curves of the other alcohols. The ethanol has less than one monolayer and the desorption from the lowest energy sites is greatly reduced. The relative amounts of each compound were determined by integrating the areas of the corrected EGA curves (see Figs. 8 and 9) and used with the mass loss data to determine the mass of each evolved compound. The relative amounts evolved also changed depending upon the amount of alcohol adsorbed on the surface. Typical results for the amount of alcohol adsorbed and the amounts of alcohol and reaction products desorbed from well-pumped samples that should have near monolayer coverage are summarized in Tables 1 and 2. The Arrhenius parameters for the evolution of the dialkylether and the evolution of the alkene were determined using first order desorption kinetics (see Figs. 10 and 11). These results are given in Tables 3 and 4.

The mass of the alcohol adsorbed on the sample was determined by weighing the sample immediately prior to and immediately after determining the TPD for the sample. Although the mass of alcohol adsorbed per gram of alumina increased as the molar mass of the sample increased, the mole percentage remained approximately constant for all of the alcohols except ethanol, which was approximately 10% lower. This indicated that except for ethanol, the number of molecules adsorbed on the surface was approximately constant for all of the alcohols examined. An estimate of the surface area covered by methanol at this coverage was made by using semi-empirical molecular orbital calculations to determine the area of a methanol molecule. The value obtained (−210 m²/g Al₂O₃) agreed well with the area

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Mass (alcohol/Al₂O₃)</th>
<th>Moles alcohol/mass Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.027</td>
<td>8.4 × 10⁻⁴</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.034</td>
<td>7.4 × 10⁻⁴</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>0.050</td>
<td>8.2 × 10⁻⁴</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>0.059</td>
<td>8.0 × 10⁻⁴</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>0.080</td>
<td>8.0 × 10⁻⁴</td>
</tr>
</tbody>
</table>

Table 1

Typical masses and number of moles of the C₁–C₅ alcohols adsorbed per mole of alumina at maximum monolayer coverage.

Fig. 7. The desorption profiles observed for the desorption of 1-propanol, dipentyl ether, 1-pentene, and the total intensity of all of the evolved gases from alumina. The sample was heated from 300 to 700 K at 7 K/min.

Fig. 8. Corrected IR intensities observed for the evolution of the gaseous products from ethanol adsorbed on alumina as a function of temperature. The relative amounts of each product produced can be determined by integrating the area under these curves.
measurement made for the acid sites using ammonia and using water (225 ± 25 m<sup>2</sup>/g Al<sub>2</sub>O<sub>3</sub>). This suggested that the methanol adsorbed on the acid sites and only a monolayer had adsorbed for well-pumped samples. Since the C<sub>3</sub>–C<sub>5</sub> alcohols have similar numbers of molecules adsorbed to the surface, it is likely that each molecule is occupying approximately the same area on the surface as methanol, i.e. it is likely that they adsorb with the remaining hydrocarbon tail extending perpendicular to the surface. There are two possible explanations for the lower amounts of ethanol adsorbed on the surface. The favored one is that since 95% ethanol was used to make the sample, some of the sites were occupied by water. The second possibility is that the hydrocarbon tail in ethanol is lying along the surface.

It has been well established that the nature of the catalyst and the reactant partial pressure will change the product ratio and the activation energies observed for the reaction [1–9]. Although between 30 and 40% of the adsorbed alcohol was converted to products for all of the alcohols examined, the mass of ether produced/g Al<sub>2</sub>O<sub>3</sub> decreased slightly for the C<sub>1</sub>–C<sub>4</sub> alcohols while the mass of the alkene/g ether mass increased for the C<sub>1</sub>–C<sub>4</sub> alcohols while the mass of the alkene/g Al<sub>2</sub>O<sub>3</sub> increased for the C<sub>1</sub>–C<sub>4</sub> alcohols.

### Table 2

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Ether (%)</th>
<th>Mass ether/g Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Alkene (%)</th>
<th>Mass alkene/g Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Alkene/ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>35</td>
<td>1.0 × 10&lt;sup&gt;−2&lt;/sup&gt;</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>12.4</td>
<td>4.0 × 10&lt;sup&gt;−3&lt;/sup&gt;</td>
<td>17.0</td>
<td>6.2 × 10&lt;sup&gt;−2&lt;/sup&gt;</td>
<td>1.4</td>
</tr>
<tr>
<td>Propanol</td>
<td>7.4</td>
<td>3.7 × 10&lt;sup&gt;−3&lt;/sup&gt;</td>
<td>22.4</td>
<td>1.1 × 10&lt;sup&gt;−2&lt;/sup&gt;</td>
<td>3.0</td>
</tr>
<tr>
<td>Butanol</td>
<td>4.4</td>
<td>2.6 × 10&lt;sup&gt;−3&lt;/sup&gt;</td>
<td>30.6</td>
<td>1.8 × 10&lt;sup&gt;−2&lt;/sup&gt;</td>
<td>7.0</td>
</tr>
<tr>
<td>Pentanol</td>
<td>4.2</td>
<td>3.0 × 10&lt;sup&gt;−3&lt;/sup&gt;</td>
<td>36.6</td>
<td>2.5 × 10&lt;sup&gt;−3&lt;/sup&gt;</td>
<td>8.6</td>
</tr>
</tbody>
</table>

The percentages are based upon the total mass of alcohol adsorbed.

The approximate percentages and the masses of the products observed for the chemical reactions during the thermal desorption of the primary alcohols on calcined boehmite.

### Table 3

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Temperature range (K)</th>
<th>A (g alkene/g Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;/min)</th>
<th>E&lt;sub&gt;a&lt;/sub&gt; (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>475–625</td>
<td>5 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
<td>92 (98)&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ethanol</td>
<td>475–625</td>
<td>4 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
<td>105 (95)&lt;sup&gt;1&lt;/sup&gt;</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>460–580</td>
<td>8 × 10&lt;sup&gt;−5&lt;/sup&gt;</td>
<td>101 (72)&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>500–620</td>
<td>1 × 10&lt;sup&gt;−4&lt;/sup&gt;</td>
<td>100</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>460–580</td>
<td>7 × 10&lt;sup&gt;−4&lt;/sup&gt;</td>
<td>103</td>
</tr>
</tbody>
</table>

Literature values for the activation energy from kinetic data are given in parentheses. The uncertainties in E<sub>a</sub> are ±10 kJ/mol and the uncertainty in A could be at least a factor of 2.

* Second order.
Table 4
First order Arrhenius constants for the desorption of the alkene produced from the alcohol adsorbed on amorphous alumina

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Temperature range (K)</th>
<th>A (g Alkene/g Al₂O₃)/min</th>
<th>Eₐ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>570–680</td>
<td>1 × 10⁸</td>
<td>132 (134)²</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>500–620</td>
<td>1 × 10⁹</td>
<td>128 (134)⁸</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>520–660</td>
<td>1 × 10⁹</td>
<td>132</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>500–620</td>
<td>1 × 10¹⁰</td>
<td>134</td>
</tr>
</tbody>
</table>

Literature values for the activation energy from kinetic data are given in parentheses. The uncertainties in Eₐ are ∼±10 kJ/mol and the uncertainty in A could be at least a factor of 2.

Al₂O₃ increased. Since the apparent activation energies for desorption of the ether and for the alkene were the same within experimental error for all of the alcohols tested and the frequency factors varied more but did not clearly follow any pattern, the cause of these differences in surface reactivity is not clear. One possible explanation is that the increased tail lengths hinder the formation of the ether. This steric effect could also explain why only 2-propanol was found to produce ether during the desorption of secondary alcohols from alumina [10,11]. However, better frequency factors will be needed to verify this hypothesis.

Based on these results, TPD-FTIR can be used to screen compounds for catalytic activity and may offer insight into the mechanisms of the chemical reactions. The activation energies observed for the formation of the products often agreed with those observed from rigorous kinetic studies [8,23]. The product ratios desorbing at each temperature can be estimated from the IR spectrum obtained at that temperature as shown in Figs. 8 and 9. The products observed agreed well with the results reported previously using other methods [1–9]. Once temperature ranges where the desired product desorbs from the catalyst have been identified, additional kinetics experiments can be done to determine if the process has industrial potential.

The hydrated alumina surface has Lewis acid, Lewis base, and Lowry-Broensted acid adsorption sites and each has been proposed as the main catalytic sites for the de-hydration of alcohols [1–9]. Semi-empirical Hartree-Fock type calculations (PM₃) were used to investigate the possible interactions between methanol and the double oxygen bridged Al₂O₂(OH)₂ molecule chosen to represent the possible surface sites to see if additional information could be obtained about the catalytic sites. Small differences in energy were observed when the methanol bonded to the different oxygen atoms on the surface, bonded to one aluminum or formed a bridge between two aluminums, and for different orientations of the oxygen or hydrogen atoms along the surface. However, since these low-level calculations are only expected to provide an indication of the relative stabilities of the possible bonding sites, these small differences were not explored in detail, but they would pro...

Fig. 11. Arrhenius plot for the production of ethene during the TPD of ethanol from alumina.

![Fig. 11. Arrhenius plot for the production of ethene during the TPD of ethanol from alumina.](image)

Table 4
First order Arrhenius constants for the desorption of the alkene produced from the alcohol adsorbed on amorphous alumina

<table>
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<th>Eₐ (kJ/mol)</th>
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<tbody>
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<td>1 × 10⁸</td>
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Literature values for the activation energy from kinetic data are given in parentheses. The uncertainties in Eₐ are ∼±10 kJ/mol and the uncertainty in A could be at least a factor of 2.

![Fig. 12. Calculated enthalpies of formation for the interaction between methanol and a model boehmite surface.](image)
vide one possible explanation for the multiple bonding sites found in the TPD experiments. Representative schematic structures and typical enthalpies of formation for that type of interaction between one methanol molecule and various atoms on the model surfaces are given in Fig. 12. Several structures and typical enthalpies of formation for that type (Lewis base site) to form an adsorbed water molecule.

Transfer of a proton from the adsorbed methanol to an oxygen in methanol and the aluminum atoms on the surface produced estimated surface interaction enthalpies between −60 and −70 kJ/mol, which is of the same order of magnitude as the experimental value. While this supports the conclusion that the reaction occurs on coupled surface acid–base sites, additional calculations will be needed to test possible coupling mechanisms and to determine if these results also hold for the other alcohols. These calculations will be the subject of a future investigation.

Acknowledgements

The authors gratefully thank the NSF-REU program (NSF-REU-0097448, and NSF-REU-0097449) and the NSF-RUI program (NSF-CHE-0076685) for supporting this research.

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