

**MASS SPECTROMETRIC ANALYSIS OF THE REACTION OF ISOTOPICALLY LABELLED ALCOHOLS ON GAMMA ALUMINA AND MODIFIED ALUMINA MATERIALS**

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**INTRODUCTION**

A novel temperature programmed desorption (TPD) technique has been developed in which the direct insertion probe of a mass spectrometer is used as the reactor. This technique has been used to investigate the adsorption sites of alcohols on gamma alumina by monitoring the dehydration products and has been found to provide both greater sensitivity and a more precise experimental record for these reactions than conventional TPD techniques. Reactions involving O-18 labelled alcohol produce two isotopomeric ether products ( $R^{18}OR$  and  $R^{16}OR$ ), in addition to  $H_2^{18}O$ , and alkene. This shows that the alcohol is initially chemisorbed onto the  $Al_2O_3$  to form alkoxides via two routes, a) a dissociative adsorption on Lewis acid sites, and b) a nucleophilic attack by a surface oxide on an alcohol which is probably activated toward C-O cleavage.

Experiments involving either poisoning the alumina with 2,6-dimethylpyridine or modifying the alumina with fluorine treatments have been used to elucidate the mechanism of alkoxide formation and the dehydration reactions. Observed product distributions and temperature trends can be related to changes in the nature of the Lewis and Bronsted acid sites brought about by the inductive effect of fluorine and to site blocking by bulk  $AlF_3$  phases or dimethylpyridine.

**EXPERIMENT**

Both a Finnigan-MAT TSQ70, operating in a single quadrupole mode, and SSQ710 mass spectrometer were used. Both instruments were operated under electron impact conditions with a 70 eV ionizing potential and 200 ua ion current. The source temperature was 150°C. A mass range from 12 to 170 Daltons was scanned every 0.5 seconds.

Norton 6375C (20/40 mesh) gamma alumina with a surface area of 221.8  $m^2/g$  and a pore volume 1.4 cc/g was used for all experiments. The gamma alumina was calcined in flowing air (60 cc/min) at 500°C for 3 h and then stored in an air tight container. Approximately 0.2 g of the alumina was then transferred to a 5-ml beaker which was placed into a 25-ml sealed vessel containing about 0.5 ml of ethanol or ethanol- $^{18}O$  (99%) at room temperature and exposed to its vapor for at least 1 h. About 0.2 mg of the alumina with the absorbed alcohol was placed into a quartz insertion tube which loaded into the temperature programmed probe of the mass spectrometer. Immediately the probe was inserted into the mass spectrometer source, which is at a vacuum of  $1 \times 10^{-7}$  torr. The temperature of the sample was increased from 25°C to 300°C at a rate of 25°C per min. The probe tip was within 1 mm of the ionizing electrons which ensures that the desorbed species are immediately analyzed upon desorption from the alumina surface. This results in minimal diffusion losses and time delays and is therefore much more sensitive than conventional temperature programmed experiments.

For the experiment involving poisoning with 2,6-dimethylpyridine,

the calcined alumina was exposed to its vapor for 24 h. The poisoned alumina was then transferred to a clean vessel and exposed to the vapors of 0.5 ml ethanol- $^{18}\text{O}$ . For the experiments involving modified alumina with fluorine loading, the alumina was treated with ammonium fluoride at 2%, 5%, and 10% levels and then calcined before exposure to the alcohol.

#### RESULTS AND DISCUSSION

Reconstructed partial ion chromatograms of the reaction of ethanol (not enriched in  $^{18}\text{O}$ ) on calcined alumina are shown in Figure 1. At 25°C only desorption of physisorbed water and ethanol is observed as shown in the selected ion traces of  $m/z = 17, 18$  and  $m/z = 45, 46$ . The physisorbed water and ethanol is rapidly evolved in the vacuum of the mass spectrometer. As the temperature is increased to 100°C, diethyl ether begins to form and reaches a maximum at 200°C. This is shown in the selected ion trace  $m/z = 59, 74$ . At 210°C ethene starts to form, peaking at 260°C (selected ion trace  $m/z = 26, 28$ ). These products are the result of dehydration reactions involving ethoxide. The coproduction of water is seen in the  $m/z = 17, 18$  ion trace, which shows a broad peak with inflections corresponding to the formation of the ether and the ethene. The ether formation is a bimolecular reaction requiring the alkoxide groups to be on adjacent sites, while the alkene is presumably formed by the unimolecular elimination of water from isolated ethoxide species.<sup>1</sup>

The same experimental procedure was repeated substituting ethanol- $^{18}\text{O}$ . The ether formation splits into distinct regions as indicated in figure 2. The reaction produces two isotopomeric ether products as evidenced by the selected ion chromatograms for  $m/z = 59, 74$  and  $m/z = 61, 76$ , which correspond to  $\text{CH}_3\text{CH}_2^{18}\text{OCH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2^{16}\text{OCH}_2\text{CH}_3$ , respectively. The ether incorporating the  $^{18}\text{O}$  appears first and peaks at 179°C. The  $^{16}\text{O}$  ether does not reach its maximum intensity until 220°C. A summary of the peak temperatures and peak areas appear in Table I. The relative amounts of these isotopomers did not change even after the  $\text{Al}_2\text{O}_3$ -ethanol- $^{18}\text{O}$  was allowed to stand for several months. This indicates that the alkoxides leading to the ether products are irreversibly formed.

The two isotopomeric ethers originate from two different alkoxide species, one incorporating an  $^{18}\text{O}$  and the other,  $^{16}\text{O}$ . The presence of these two alkoxides suggest that alkoxide is formed via two routes. The first involves a direct reaction at a Lewis site resulting in deprotonation of the complexed alcohol and formation of  $^{18}\text{O}$ -alkoxide as shown in the upper scheme in figure 2. The second involves a reaction with a nucleophilic surface base site resulting in  $^{18}\text{OH}$  displacement and the formation of  $^{16}\text{O}$ -alkoxide, as shown in the lower scheme in figure 2. This latter pathway probably involves a secondary interaction of the alcohol hydroxyl with an adjacent acid site, since hydroxide itself is a relatively poor leaving group.

The 2,6-dimethylpyridine poisoning experiment provides further evidence for the formation of distinct alkoxide sites. This base is expected to adsorb onto either Bronsted acid sites or Lewis acid sites.<sup>2</sup> The adsorption of 2,6-dimethylpyridine prior to ethanol- $^{18}\text{O}$  adsorption has a significant effect on the ratio of ether- $^{18}\text{O}$  and ether- $^{16}\text{O}$  as shown in Table I. The untreated alumina yields ethers approximately 3:1 in favor of the  $^{18}\text{O}$  isotopomer. This ether ratio

changes to 0.6:1 for the base treated alumina. This clearly establishes that both ethers are formed from different alkoxide species and that the ether-<sup>18</sup>O is formed from an alkoxide associated with Lewis acid sites. It also shows that the relative amount of the ether-<sup>18</sup>O to the ethene actually is increased by effect of the 2,6-dimethylpyridine poisoning. This result also indicate that the ether-<sup>18</sup>O did not form at a Bronsted acid site (via protonolysis of alcohol hydroxide), since the latter would be strongly inhibited by the pretreatment with 2,6-dimethylpyridine; this would have led to a decrease in the ratio of ether-<sup>18</sup>O to ethene, rather than the observed increase.

Modification of alumina by fluorine treatment is known to increase the Bronsted acid character of the surface.<sup>3</sup> At 2% fluorine loadings the observed ether and ethene distributions show no significant changes, although the peak temperatures of various reactions

increased substantially, probably due to the the inductive effect of the fluorine. (Table I) At the 5% fluorine level the peak temperatures have increased to the point of favoring elimination as the major reaction pathway. The yield of the ether-<sup>18</sup>O is greatly reduced since the fluorine is now occupying sites previously occupied by the <sup>18</sup>O ethoxide. At the 10% fluorine level even the ether-<sup>18</sup>O is reduced. This can be attributed to site blocking due to the formation of bulk AlF<sub>3</sub> on the alumina surface.

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2. Matulewicz, E. R. A., Kerhof, F. P. J. M., Moulign, J. A. and Reitsma, H. J., J. Coll. Interface Sci., 77, 110 (1980).

3. Ghosh, A. K, and Kydd, R. A., Catal. Rev. [Sci. Eng., 27 [4], 539-589 [1985]

TABLE I  
PEAK TEMPERATURES AND PRODUCT DISTRIBUTIONS  
FOR ETHANOL-<sup>18</sup>O ON ALUMINA AND MODIFIED ALUMINA

ALUMINA	PRODUCT	PEAK TEMP	Ethene to Et <sup>18</sup> OEt	Ethene to Et <sup>16</sup> OEt	Et <sup>18</sup> OEt to Et <sup>16</sup> OEt
UNTREATED	Et <sup>18</sup> OEt	179	22	69	3.2
	Et <sup>16</sup> OEt	220			
	Ethene	261			
2,6-DIMETHYL PYRIDINE	Et <sup>18</sup> OEt	220	36	23	.62
	Et <sup>16</sup> OEt	275			
	Ethene	286			
2% FLUORINE	Et <sup>18</sup> OEt	240	20	58	3.0
	Et <sup>16</sup> OEt	266			
	Ethene	295			
5% FLUORINE	Et <sup>18</sup> OEt	256	260	86	.32
	Et <sup>16</sup> OEt	269			
	Ethene	285			
10% FLUORINE	Et <sup>18</sup> OEt	260	120	290	2.4
	Et <sup>16</sup> OEt	280			
	Ethene	287			

FIGURE 1

ETHANOL

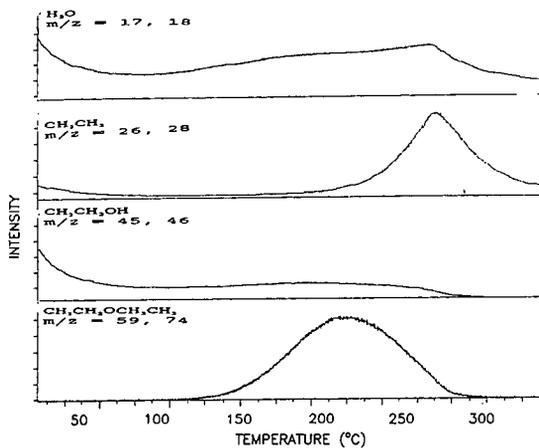


FIGURE 2

ETHANOL- $^{18}\text{O}$

