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Influence of Pretreatment of Alumina on the Dehydrogenation: Dehydration Selectivity for 2-Octanol

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INTRODUCTION

The conversion of 2-octanol over thoria catalysts proceeded by two reaction pathways: dehydration to octenes and dehydrogenation to 2-octanone (*1*). The two pathways were sensitive to catalyst pretreatment and catalyst preparation method with the catalyst pretreatment predominating in the selectivity determination. It was of interest to extend this study to other insulator-type metal oxide catalysts since this type of selectivity is expected only for typical semiconductor catalysts. This paper reports some results for the conversion of 2-octanol over alumina which is usually viewed as a very selective dehydration catalyst (*2*).

EXPERIMENTAL METHODS

Catalysts

Al_2O_3–A. This alumina was prepared by the hydrolysis of aluminum isopropoxide with water (*3*). After activation at 600°C in air the surface area was 200 m^2/g.

Al_2O_3–K. 99.99% Aluminum was dissolved in KOH. After adding HNO_3 to incipient precipitation, CO_2 was bubbled into the solution to effect complete precipitation (*3*). The catalyst contained 0.1% K and the surface area was 200 m^2/g after calcination at 600°C.

Al_2O_3–Hg. Aluminum was amalgamated using $HgCl_2$ (*4*). The temperature during the preparation was 25–40°C.

Al_2O_3–Cl. Alumina was precipitated from a 33 wt % aluminum chloride solution using ammonium hydroxide. The catalyst was washed until the wash water gave a negative chloride test with $AgNO_3$. After calcination at 600°C in air the catalyst contained 0.5% Cl.

Reaction Runs

The catalyst was treated *in situ* at 600°C with either flowing hydrogen or oxygen for 4 hr. The catalyst was cooled to the reaction temperature in about 15 min in a flow of the pretreatment gas. The reactant was fed to the catalyst with a syringe pump. The reaction was carried out at 180°C (250°C for Al_2O_3–K), LHSV 0.3, 5 cm^3 catalyst (2.5 g), and no carrier gas. Liquid samples were collected at intervals and analyzed by gc using Carbowax 20M and a temperature programmed at 15°/min from 60 to 250°C.

RESULTS

Results for the conversion of 2-octanol over four alumina catalysts pretreated with hydrogen or with oxygen are presented in Table 1. It is noted that the selectivity for dehydrogenation and dehydration depends on the catalyst pretreatment. For all four catalyst preparations, the amount of dehydrogenation is 4–8 times greater for the oxygen pretreated sample than for the hydrogen pretreated sample. In addition, the dehydration activity of the oxygen pretreated sample is lower than the hydrogen pretreated sample by a factor of 2–4. Thus, the selectivity defined by dehydration/dehydrogenation is considerably different for the two catalyst pre-

TABLE 1

PRODUCT DISTRIBUTION FROM THE CONVERSION OF 2-OCTANOL OVER ALUMINA PRETREATED WITH HYDROGEN OR OXYGEN

	Hydrogen				Oxygen				Selectivity (olefin/ketone)	
Catalyst	Time on stream (min)	Octenes	2-Octanone	?	Time on stream (min)	Octenes	2-Octanone	?	Hydrogen pretreatment	Oxygen pretreatment
Al_2O_3-A	72	83	1.7	1.1	99	16	18	1.4	48	0.9
	113	44	2.5	6.0	135	13	13	1.1	18	1.0
	160	34	2.6	5.8	171	12	10	1.9	13	1.2
	234	32	2.8	6.6	221	12	10	2.6	11	1.2
Al_2O_3-Hg	86	79[a]	4.6	—	95	32[a]	16	—	17	2.0
	131	40	10	5.0	145	30	13	3.3	4.0	2.3
	169	36	9.6	5.8	175	15	12	3.3	3.8	1.3
	232	31	9.8	7.6						
Al_2O_3-Cl	85	78	1.9	—	90	53	12	—	42	4.4
	125	35	3.8	—	145	29	13	—	9.2	2.2
	158	29	3.6	4.7	195	25	6.1	4.9	8.1	4.0
	210	28	3.5	8.0	225	21	5.1	6.3	8.0	4.1
Al_2O_3-K	56	54	4.5	—	52	44	21	1.1	12	2.1
	91	36	6.1	1.2	83	31	13	2.0	5.9	2.4
	141	43	5.9	1.6	125	35	11	3.0	7.3	3.2
	186	43	5.8	2.2	177	34	6.7	2.5	7.4	5.1
	236	41	6.3	1.8	240	37	5.6	3.7	6.5	6.6
	Air at 600°C, then H_2 at 550°C									
Al_2O_3-K	45	67	7.7	—					8.7	
	93	59	8.1	1.4					7.3	
	136	51	8.9	1.3					5.7	
	174	48	9.0	2.3					5.3	
	228	51	9.1	2.6					5.6	

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[a] Octane was also present in the products from the hydrogen pretreated catalyst but not from the oxygen pretreated catalyst (sample 1 contained about 21% octane; samples 2, 3, and 4 about 2%).

treatments (columns 10 and 11, Table 1).

The dehydration/dehydrogenation selectivity S also depends on the source of the alumina. The largest dependence on pretreatment was for the acidic Al_2O_3–A where S ranged (neglecting the first sample) from 17 to 11 for the hydrogen pretreated catalyst and from 1 to 1.2 for the oxygen pretreated catalyst. For the other three catalysts S for the hydrogen and oxygen pretreated samples were: Al_2O_3–K, 6–6.5 and 2.3–6.5; Al_2O_3–Cl, 8–9 and 1.4–4; Al_2O_3–Hg, 2.1–4 and 1.3–2. Thus, the catalysts can be put in the order: $Al_2O_3\text{–A} > Al_2O_3\text{–K} \simeq Al_2O_3\text{–Cl} > Al_2O_3\text{–Hg}$ for the change in S in changing from a hydrogen to an oxygen pretreatment. Also the four catalysts' selectivity changes differently with time on stream; the Al_2O_3–A catalyst changes very slowly but after 200 min on stream the Al_2O_3–Hg and Al_2O_3–K catalysts approached a similar selectivity for both pretreatments.

For Al_2O_3–A, the dehydration activity of the hydrogen pretreated sample was about three times that of the oxygen pretreated sample. For Al_2O_3–Hg, the hydrogen pretreated sample was also more active for dehydration but for Al_2O_3–Cl and Al_2O_3–K the dehydration activity was about the same for both the oxygen and hydrogen pretreatment. Thus, the pretreatment also influences the dehydration activity.

DISCUSSION

Alumina is usually viewed as an extremely selective dehydration catalyst producing olefins, and at lower temperatures ethers, during the conversion of alcohols (*2*). However, there are reports that alumina has activity for dehydrogenation as well as dehydration (*5*). Our results show that alumina may be nearly as active for dehydrogenation as for dehydration.

One explanation for the dehydrogenation activity is a hydrogen transfer reaction. Alumina is a catalyst for the reaction $R_2C{=}O + R'_2CHOH \rightarrow R_2CHOH + R'_2C{=}O$. But this type of reaction is not possible in our study since no ketone is initially present. *n*-Octane was formed in some runs at early time on stream. However, the hydrogen-pretreated catalysts, which were not very active for dehydrogenation, were the only catalysts that were active for the formation of *n*-octane. Over the oxygen-pretreated sample, the amount of *n*-octane was always less than 5–10% of the amount of 2-octanone and no other hydrogen-rich material was detected which could account for the amount of 2-octanone formed. Thus, a hydrogen transfer reaction does not appear to be responsible for 2-octanone formation. Another explanation for the dehydrogenation by oxygen-pretreated samples could be the reaction: $2\ C_6H_{13}CHOHCH_3 + O_{2(ads)} \rightarrow 2\ C_6H_{13}COCH_3 + H_2O$. But a calculation for 2-octanol conversion over Al_2O_3–A indicates that this is unlikely since the amount of 2-octanone formed is too large to be due to chemisorbed oxygen. Thus, it appears that the selectivity is determined by changes in a catalyst property.

Vol'kenshtein (*6*) and Hauffe (*7*) have advanced theories leading to opposing conclusions for selectivity dependence on the Fermi Level of semiconductors. Vol'kenshtein's theory predicts that a lowering of the Fermi level would poison dehydrogenation and stimulate dehydration while displacement of the Fermi level upwards would have the opposite effect. On the other hand, Hauffe's theory indicates that lowering the Fermi level would enhance dehydrogenation and reduce dehydration.

The electronic properties of alumina have not been widely studied. Khoobiar, Carter, and Lucchesi (*8*) studied the influence of hydrogen or oxygen on the electronic properties of η-alumina at 600°C, the temperature used for the pretreatment in the present study. An increase in hydrogen or oxygen pressure caused a corresponding linear increase in the dc conductivity; furthermore, the conductivity of alumina in the hydrogen atmosphere was of the *n*-type whereas in an oxygen atmosphere it was *p*-type. Weller and Montagna (*9*) have found that a hydrogen pretreatment at 550°C creates sites for hydrogen uptake at 200°C. One explanation for these results is that hydrogen reacts with alumina leading to a reduction of the alumina in the surface. In the present study the samples were treated at 600°C in 1 atm of flowing hydrogen or oxygen for 4 hr and then cooled to the reaction temperature during a 10–15 min period in the pretreatment gas flow. Thus, our alumina sample should retain electrical properties similar to those obtained by the high temperature pretreatment. It may appear that the chemical selectivity of the alumina is determined by the surface composition rather than the bulk properties. However, the X-ray crystallite size of the alumina was about 80 Å and we would expect this to be at least near a size where the surface and bulk properties are not independent.

In summary, it appear that the insulator metal oxide alumina is sensitive to pretreatment, and conductivity, in a manner parallel to that of semiconductors. This suggests that the selectivity, and hence the reaction mechanism over alumina and thoria, is determined by the electronic property of the solid. If our alumina samples have the electrical properties similar to those of Khoobiar, Carter and Lucchesi (*8*), our selectivity data agrees with Hauffe's prediction for selectivity dependence on Fermi level changes.

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