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NOTE

Conversion of Isoamyl Alcohol over Acid Catalysts: Reaction Dependence on Nature of Active Centers

Acid catalysts are known to catalyze the dehydration of alcohols (1–3). In addition some oxide catalysts with basic properties have also been shown to play an important role in such dehydration reactions (2). The dehydration of aliphatic alcohols to olefins has been studied in detail using alumina (3, 4), silica-alumina (5), and zeolite (6, 7) catalysts. The olefin products further undergo isomerization in presence of acidic sites. The reaction of isoamyl alcohol on catalytic surfaces has not been investigated in greater detail. The dehydration of isoamyl alcohol is of considerable interest in fine chemicals. Isoamyl alcohol may also undergo dehydrogenation as observed in the case of *n*-butanol (8). The scope of the present work is to identify the nature of the active sites selective for dehydration and dehydrogenation of isoamyl alcohol and to modify the active sites to promote isomerization of dehydrated products. Four catalytic surfaces on which the acidic strength can be varied, as well as selectively suppressed, are chosen for this study.

The γ-alumina catalyst used in the present study was obtained from Harshaw (111-61E, 1/16″ extrudates). For experimental studies, the γ-alumina sample was calcined in static air at 770 K for 8 h, cooled, stored, and then used. The sodium impregnated γ-alumina catalyst samples were prepared by the incipient wetness method, i.e., by keeping a known weight of alumina in a requisite amount of sodium hydroxide solution ($Na/\gamma\text{-}Al_2O_3 = 0.002$ and 0.02 on wt/wt basis). The solution was evaporated to dryness by continuous stirring. The zeolite (ZSM5) was prepared using sodium silicate, sodium aluminate, and tetrapropylammonium bromide (template) as reported earlier by Argauer and Landolt (9). The crystalline sample (confirmed by comparing with the standard XRD pattern) was calcined at 793 K to get NaZSM5 and further ion-exchanged with 10% ammonium chloride solution (twice). The NH_4ZSM5 thus obtained was analyzed by the wet chemical method and flame photometry. The SiO_2/Al_2O_3 mole ratio of the zeolite sample was 82 and the sodium content was 0.05 wt%. The NH_4ZSM5 sample was calcined in static air at 793 K for 8 h to get HZSM5 (10). Silica was prepared by the addition of dilute sulfuric acid to sodium silicate solution (final $pH = 9$). The gel was aged for 18 h at 300 K, washed free of sulphate, and dried at 383 K for 18 h. The silica powder (surface area = 179 m^2/g) was calcined in static air at 793 K before use. Active carbon (surface area = 822.4 m^2/g) was obtained from the Indian Institute of Chemical Technology, Hyderabad, in granular form. Calculated amounts of orthophosphoric acid (BDH chemicals, 85%) were added to silica or carbon to prepare the catalysts with the required composition (H_3PO_4/silica = 0.2, 0.5, and 1.0 on wt/wt basis and H_3PO_4/carbon = 1.0 on wt/wt basis) by the evaporation technique.

Acidity of the catalysts was known (11) to be determined by a pyridine adsorption method using IR technique. In our study, the weight gain of the sample due to adsorption of pyridine on acidic sites was measured by a McBain quartz balance. The catalyst powder sample was pressed to form a tablet and crushed to 10–20 mesh pellets. A catalyst sample (200 mg, 10–20 mesh) was loaded in the sample bucket and activated at 593 K under vacuum for 5 h. At 473 K, pyridine vapors ($P/Po = 0.5$) were introduced and the sample was allowed to attain equilibrium after a period of 1 h. Then the sample was evacuated at the same temperature for 1 h and the height of the quartz spring (connected to the sample bucket) was measured (using a cathetometer). The quartz spring height measured by the cathetometer in millimeter was noted as the first reading. With increase in sample temperature, the weight loss due to desorption of pyridine from the sample shows a change in the height of the spring, which was measured as a second reading. Using the standard graph of change in spring height versus the known weight of the sample in the bucket, the amount of pyridine retained by irreversible adsorption on the catalyst surface (as pyridinium ion) at two different temperatures (473 and 593 K) was measured and tabulated in Table 1. Pulse experiments were conducted in a micro reactor at 573 K and GHSV (gas hourly space velocity) of 8000–8400 h^{-1} using nitrogen as the carrier gas to study the cumene cracking activity. The reactor was made from a stainless steel tube of $\frac{1}{4}''$ O.D. and 4″ length. The catalyst sample (~20 mg) was loaded in the center of the reactor which was loosely plugged at both ends by quartz wool. The reactor was connected between the injection port and the analytical column of a gas chromatograph. A fixed bed downflow glass reactor was used to measure the conversion of isoamyl alcohol (dehydration + dehydrogenation) on various catalysts.

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TABLE 1

Irreversible Pyridine Adsorption (at P/Po = 0.5) on Fresh and Doped (with Alkali and Phosphoric acid) Catalysts Measured at Different Sample Temperatures

Catalyst	Adsorption of pyridine (mmole g^{-1} sample) 473 K	593 K	Cumene cracking (%)
γ-Al_2O_3	0.095	trace	8.1
Na/γ-Al_2O_3 (0.002)	0.053	trace	—
Na/γ-Al_2O_3 (0.02)	trace	trace	—
H_3PO_4/γ-Al_2O_3 (1.0)	1.164	0.386	7.5
silica	trace	trace	—
H_3PO_4/silica (0.2)	0.225	0.075	—
H_3PO_4/silica (0.5)	0.646	0.198	7.8
H_3PO_4/silica (1.0)	1.139	0.362	7.7
Carbon	trace	trace	—
H_3PO_4/carbon (1.0)	1.119	0.378	7.7
HZSM-5	0.312	0.227	91.3

Note. The values in parenthesis indicate dopant added to the support in wt/wt ratio.

About 10 g (10–20 mesh) of the catalyst was activated in a nitrogen atmosphere at 583 K prior to the introduction of feed at 10 g h^{-1} (weight hourly space velocity = 1.0). The liquid product was condensed at 278 K and analyzed by gas chromatography.

Silica and carbon being less acidic supports show a negligible amount of pyridine retention at 473 K compared to γ-alumina (Table 1) which is known to possess weak acid sites (12). On the other hand, sodium-doped γ-alumina showed a marked decrease in pyridine uptake, indicating a reduction in the number of acidic sites. Further, the increased pyridine uptake on phosphoric acid treated supports indicated an enhancement of the surface acidity, i.e., there is an increase in the number of acid sites. On raising the temperature to 593 K, a significant amount of pyridine was desorbed. In comparison, HZSM5, showed a lower pyridine uptake, but a significant retention of pyridine (0.227 mmoles g^{-1}) at 593 K indicating a strong acid site strength. These observations lead us to conclude that the relative acidic strength of P–OH groups of phosphoric acid treated supports was lower than the Al–OH–Si groups of HZSM5. In literature (13), the cumene cracking reaction was used to measure the acidic strength of catalysts. Therefore, in the present study a microreactor was used to determine the extent to which catalysts are active in the cumene cracking reaction. The results are shown in Table 1. It was observed that the phosphoric acid-doped catalysts are less active, compared to HZSM5 in the cumene cracking reaction. This difference in activities between HZSM5 and other catalysts arises from the differences in the strength of their acidic sites. Table 2 shows the results of alcohol dehydration activity obtained on fresh, alkali-doped and phosphoric acid-doped catalysts. Dehydration of alcohol over γ-alumina gave 3M1B (3-methyl-1-butene) as the major product and 2M2B and 2M1B (2-methyl-1-butene) as minor products. In addition, a high boiling by-product identified as isovaleric aldehyde, was also formed, probably via the

TABLE 2

Composition of the Product Obtained from the Isoamyl Alcohol Reactions on Catalysts Loaded with Different Concentrations of Dopants

Product composition (wt%)	γ-Al_2O_3	Na/γ-Al_2O_3 (0.02)	Na/γ-Al_2O_3 (0.002)	H_3PO_4/γ-Al_2O_3 (1.0)	HZSM5	HZSM5
C_1–C_4	4.30	—	0.50	5.50	6.60	14.66
3M1B	58.27	0.35	2.99	4.23	4.75	7.52
2M1B	2.90	0.03	0.35	12.68	16.18	13.25
2M2B	8.27	0.12	0.83	34.65	43.60	24.65
C_5+	2.01	—	—	7.81	16.32	37.20
Iso.alc	9.36	98.60	85.21	10.02	12.50	2.72
Iso.aldehyde	14.79	0.90	9.73	T	T	T
Iso.alc.convn.*	2.86×10^{-6}	0.04×10^{-6}	0.46×10^{-6}	2.83×10^{-6}	6.90×10^{-6}	3.06×10^{-6}
2M2B/2M1B	2.85	—	—	2.73	2.70	1.86
WHSV	1.00	1.00	1.00	1.00	2.50	1.00
DH (%)	83.69	35.72	34.22	>99.00	>99.00	>99.00
DHG (%)	16.31	64.28	65.78	<1.00	<1.00	<1.00

Note. Values in parenthesis are on wt/wt basis. Reaction temperature = 573 K. Iso.alc = Isoamyl alcohol (unreacted). Iso.aldehyde = Isovaleric aldehyde. T = Trace. DH = Dehydration selectivity. DHG = Dehydrogenation selectivity. WHSV = weight of liquid reactant fed in the reactor hour −1 ÷ weight of the catalyst. Iso.alc.convn* = Isoamyl alcohol conversion (moles of alcohol converted per gram catalyst per second).

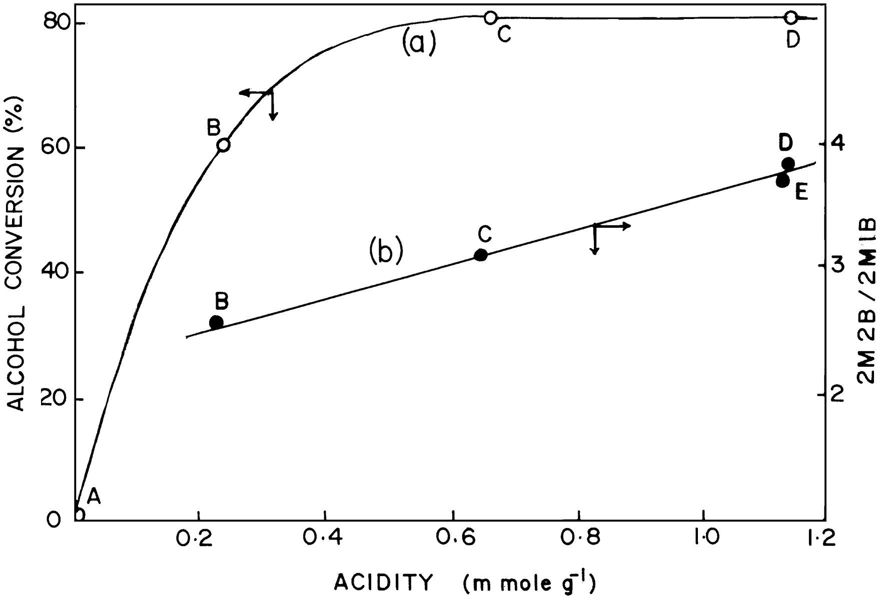

FIG. 1. (a) Isoamyl alcohol conversion as a function of surface acidity of fresh and acid doped samples, A = Silica, B = H_3PO_4/silica (0.2), C = H_3PO_4/silica (0.5), and D = H_3PO_4/silica (1.0) and (b): The ratio of isomerized products (2M2B/2M1B) as a function of surface acidity of samples, B, C, D, and E = H_3PO_4/Carbon (1.0).

dehydrogenation reaction. On sodium-doped γ-alumina it was seen that the latter reaction occurred at 65% selectivity, compared to dehydration, suggesting that dehydrogenation is preferred on relatively weak Lewis acid sites (tri-coordinated aluminum ions), whereas dehydration occurs mainly on strong acid sites (Al–OH). This observation is similar to that reported by Deo *et al.* (14), and Fiedorow *et al.* (15). Other studies on solid acid zeolite catalysts (16) also reported a dependence of the dehydration activity on strong Bronsted sites. Poisoning of these sites by basic molecules led to a drop in dehydration activity (17).

In an attempt to convert 3M1B, the major product on γ-alumina, to 2M2B, the surface acidity was altered by phosphoric acid doping. The data obtained indicated the formation of large amounts of products as a result of dehydration followed by the isomerization reaction and a negligible amount of isovaleric aldehyde (by dehydrogenation). Isoamyl alcohol conversions are listed as moles per gram catalyst per second in Table 2. However, as shown in Table 2, phosphoric acid-doped γ-alumina yielded side products viz., light olefins C1–C4 and C5+ hydrocarbons. Product analysis showed that ethylene, ethane, propane, and propylene are the major components of light olefins, whereas the C5+ consisted of pentanes, methyl pentanes, benzene, methyl hexanes, and toluene. Although the alcohol conversion occurs selectively via dehydration on phosphoric acid-doped γ-alumina, the formation of secondary reaction products reduces the yield of 2M2B formed. This can be attributed to the combined effects of the intrinsic acidity of γ-alumina and the protons of the P–OH groups.

On less acidic supports viz., silica, progressively doping with phosphoric acid enhances the alcohol conversion selectively to dehydrated/isomerized products (Fig. 1). Alcohol conversions calculated as moles per gram catalyst per second are listed in Table 3. It was also seen that increasing the phosphoric acid loading (acid/silica from 0.2 to 1.0) on silica or carbon enhanced the 2M2B formation (as seen by the increase in 2M2B/2M1B ratio from 2.58 to 3.80). HZSM5, on the other hand, although it preferentially

TABLE 3

Product Composition Obtained from Isoamyl Alcohol Reactions on Catalysts Having Different Acid to Support Ratio

Product composition (wt%)	H_3PO_4/silica (0.2)	H_3PO_4/silica (0.5)	H_3PO_4/silica (1.0)	H_3PO_4/carbon (1.0)
C_1–C_4	1.50	1.75	2.88	6.32
3M1B	3.39	4.23	2.72	3.87
2M1B	14.55	17.03	13.81	12.07
2M2B	37.55	54.02	52.57	45.01
C_5+	3.02	4.80	8.10	12.80
Iso.alc	39.90	18.18	19.90	19.89
Iso.alc.convn.*	1.89×10^{-6}	2.58×10^{-6}	2.52×10^{-6}	2.52×10^{-6}
2M2B/2M1B	2.58	3.17	3.80	3.73
WHSV	1.00	1.00	1.00	1.00

Values in parenthesis are on wt/wt basis. Reaction temperature = 503 K. WHSV = weight of liquid reactant fed in the reactor/hour ÷ weight of the catalyst. Iso.alc.convn* = Isoamyl alcohol conversion (moles of alcohol converted per gram catalyst per second).

dehydrates/isomerizes (Tabel 2), gives very low 2M2B yields even at higher values of WHSV (2.50). Increasing the reaction contact time (by decreasing WHSV from 2.50 to 1.00) with the view of enhancing the 2M2B/2M1B ratio only resulted in the formation of large amounts of C5+ hydrocarbons via disproportionation, oligomerization, and cracking of olefins. Dehydrogenation was not observed, further confirming that strong acid centers of ZSM5 are not the preferred sites for this reaction. Based on these observations and discussions presented, it can be concluded that the dehydration and isomerization reactions of isoamyl alcohol to give high yields of 2M2B can be achieved preferably on acid sites (P–OH) of moderate strength generated by phosphoric acid doping on less acidic supports such as silica or carbon.

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