

Preparation, Characterization, and Comparison of Properties of Alumina Catalysts

The catalytic activity of alumina is influenced by the conditions at which it is prepared such as preheating time and temperature (1-4), final calcination temperature, precipitation and ageing of the hydroxide (5-7), and the source (1) from which alumina is obtained. The various commercially available catalysts exhibit wide variations in their activity and selectivity. However, the most important methods in practice for the laboratory preparation of alumina catalysts are (1) hydrolysis of an aluminum salt usually the nitrate using aqueous ammonia (1), (2) hydrolysis of an aluminum isopropoxide by water (1), and (3) decomposition of aqueous Na/K-aluminate by CO₂ (1). These procedures give the hydroxide in the form of gel, whose filtration and washing are cumbersome and time-consuming processes. The present paper reports the preparation of *two* types of alumina catalyst from aluminum isopropoxide. These are (1) slow hydrolysis of aluminum isopropoxide [Catalyst-3] (a much simplified version of the aerogel method (8)) and (2) thermal decomposition of aluminum isopropoxide [Catalyst-2].

Aluminum isopropoxide is a desirable starting material for the preparation of pure alumina, since it can be readily prepared from pure aluminum metal and can be further purified by vacuum distillation. The methods reported here do not involve filtration and results obtained with them were all reproducible. Both the catalysts are active for conventional alumina-catalyzed reactions, but differ in their selectivity. The catalysts have been characterized by their crystallinity, structure, surface area, pore-

size distribution, and pore volume by conventional nitrogen adsorption-desorption method. The observed activity and selectivity are compared with those of alumina samples prepared by the conventional method (catalyst-1, hydrolysis of aluminum isopropoxide by water (1)) and also with a commercial catalyst (catalyst-4). A comparative study of the reactions of benzyl alcohol over these catalysts has been reported earlier (9).

EXPERIMENTAL

Alumina catalyst-1 was prepared by the hydrolysis of double-distilled aluminum isopropoxide by water (1). The hydroxide was filtered-washed, dried at 120°C for 12 h, and calcined at 600°C for 6 h.

Alumina catalyst-2 Double-distilled aluminum isopropoxide (10) 100 g was taken in a 500-ml RB flask fitted with an air condenser and a calcium chloride guard tube. The aluminum isopropoxide was then refluxed on a sand bath whose temperature was kept at 400-450°C until all the aluminum isopropoxide was decomposed to white flake-like solid (nearly 3-4 h). The flakes were scraped, taken in a silica crucible, and calcined at 600°C for 6 h in a muffle furnace. The alumina thus obtained weighed 23 g (~100% in yield). It was observed that if the same experiment was carried out in a smaller flask, the alumina was found to be contaminated with carbon deposits (probably due to the polymerization and decomposition of propene produced in the reaction).

Alumina sample 3. Double-distilled aluminum isopropoxide 204 g (1 mole) was

taken in a wide porcelain dish such that the liquid formed a 1- to 2-cm-thick layer and was exposed to the atmosphere (relative humidity 50–70%) for 48 h. The porcelain container was kept covered by a cloth to prevent contamination by dust from the atmosphere. As the hydrolysis by atmospheric moisture progressed, the crust was broken up periodically with a glass rod. The lumps formed were scraped and taken up in a silica crucible. This was heated initially in an air oven at 120°C for 12 h. and then calcined at 600°C for 6 h. The white powder so obtained weighed 55 g (~100% in yield).

Alumina catalyst-4 was a commercial catalyst (Houdry Hard G 200 A).

The values of surface area and pore-size distribution of these samples were computed from nitrogen adsorption and desorption isotherms. Acidity measurements were done by *n*-butylamine adsorption methods (11). The general experimental technique and the flow reactor used have already been described (12).

RESULTS AND DISCUSSIONS

The values of total acidity (as determined by *n*-butylamine adsorption), surface area, average pore radius, specific pore volume, and pore size distribution in terms of percentage pore volume in the range 2–20 nm are shown in Table 1. Sample-3 and sample-1 have nearly the same total pore volume. However, there is a drastic change in the distribution of the pore size. Though the sample-2 has less total pore volume compared to the other samples the pore size distribution is similar to that of sample-3. Samples-2 and -3 are rich in mesopores (5–10 nm) and the sample-1 is rich in micropores (below 2 nm).

The diffraction pattern of the sample-3 has a clear indication of the crystalline modification of η -alumina (13), though the presence of small amount of γ -alumina is not ruled out. The samples-1 and -2 predominantly have γ -alumina modification in addition to small amounts of other modifications.

TABLE I
Characterization of Alumina Samples

No.	Condition	Samples			
		1	2	3	4
1.	Total acidity [(eq/g) $\times 10^{-4}$]	7.01	4.77	6.38	4.01
2.	Surface area (m ² /g)	174	120	229	165
3.	Average pore radius (nm)	8.3	6.4	6.2	—
4.	Sp. pore volume (ml/g)	0.72	0.33	0.71	—
5.	Pore radius distribution in terms of % pore volume				
	Radius range	% Distribution			
		Sample 1	Sample 2	Sample 3	
2		23	17	18	
3–4		16.6	12.8	9.7	
4–5		9	11	9.7	
5–10		17.9	31.9	38.4	
10–20		16.6	10.6	11.7	
20		—	4.3	—	

Activity and Selectivity

A comparative study on the activity and selectivity of these alumina samples has been carried out and the results are summarized in Table 2. It is clear from the results that in the dehydration of ethanol, alumina sample-3 is more active and selective toward olefin formation. Sample-1 (conventional alumina) is qualitatively similar in activity and selectivity as sample-3, sample-2 is more selective toward ether formation. Sample-4 (commercial sample) is least active compared to other alumina samples. Studies on the dehydration of isopropanol (not reported here) also showed qualitatively similar results. These results are in accordance with our earlier observations (9) that in the reaction of benzyl alcohol sample-2 is selective for ether formation whereas samples-1 and -3 are selective for disproportionation of benzyl alcohol to toluene and benzaldehyde.

Results of the reaction of cyclohexene (Table 2) shows that alumina samples-1 and -3 are active for isomerization whereas samples-2 and -4 are inactive under the reaction conditions.

To compare the dehydration versus hydride-transfer activity (14) of these sam-

TABLE 2
Reactivity and Selectivity of Alumina Sample

No.	Reactant	Product	Catalyst sample			
			1	2	3	4
Mole % of products						
1. Ethanol ^a		Ethane	60	28	73	2
		Ether	13	34	8	6
		Total conversion	75	63	83	10
2. Cyclohexene ^b		Total conversion				
		(methylcyclopentenes)	20	—	24	—
3. Isopropanol + acetophenone ^c		Styrene ^d	58	71	38	65
		Acetophenone ^d	41	26	60	30
		Acetone ^e	56	70	34	62
		Propene ^e	25	26	62	15
		Isopropanol ^e	15	Trace	Trace	25
	Diisopropyl ether ^e	1	2	—	1	

^a Catalyst weight, 1 g; Temperature, 350°C; Flow rate, 20 ml/h; Reactant, 10 ml of ethanol (neat).

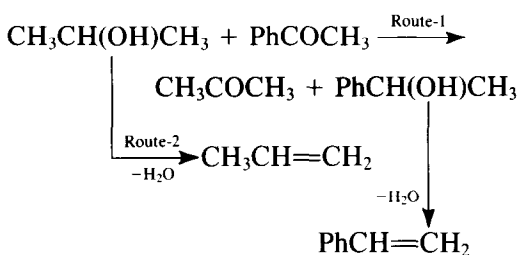
^b Catalyst weight, 1 g; Temperature, 400°C; Flow rate, 10 ml/h; Reactant, 10 ml of cyclohexene (neat).

^c Catalyst weight, 1 g; Temperature, 350°C; Flow rate, 10 ml/h; Reactant, 8.6×10^{-3} mole of 1:1 molar solution of isopropanol and acetophenone.

^d Based on acetophenone taken initially.

^e Based on isopropanol taken initially.

ples, the reaction of acetophenone with isopropanol has been studied and results are summarized in Table 2.



Here it may be noted that styrene arises by the hydride transfer from isopropanol to acetophenone followed by the dehydration of the methylphenylcarbinol (Route-1). Acetone and styrene are formed in equal quantities. Propene on the other hand is formed from the straight dehydration of isopropanol. Thus the ratio propene versus acetone or styrene gives the selectivity for dehydration versus hydride transfer. The results show that alumina samples-3 and -1

are more selective toward dehydration of isopropanol than for the hydride transfer from isopropanol to acetophenone, whereas samples-2 and -4 are more selective toward the hydride transfer than for the dehydration. In all these samples of alumina only trace amounts of methylphenylcarbinol are found. It seems that the methylphenylcarbinol formed in the reaction has undergone dehydration to styrene under the reaction conditions.

Thus from these studies, it is concluded that alumina sample-2 is more selective for ether formation in the dehydration of alcohols and less active for the isomerization of olefins. Sample-3 is more active as well as selective in the dehydration of alcohol to olefins and for the isomerization of olefins. From the earlier studies (9), it is well established that alumina sample-3 is rich in strong acid sites whereas sample-2 is rich in weak acid sites. It can be concluded that the difference in the activity and selectivity

arises due to the distribution of active sites with different strength.

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