

## Hydride Transfer Reactions

VIII. Reactions of Benzyl Alcohol Over Alumina: Dehydration and Disproportionation<sup>1</sup>

The present study is a continuation of the study of the disproportionation of diphenylcarbinol over alumina (1). Landis and Heiba (2) had reported the disproportionation of benzyl alcohol over alumina to yield benzaldehyde, toluene, and water, in addition to the expected dehydration to the ether. In the present paper an attempt is made to differentiate the sites responsible for disproportionation and dehydration.

Alumina catalysts were prepared by different methods of which three sources yielded catalysts with significantly different selectivities. These were the following: (1) Conventional catalyst, prepared by the calcination of precipitated aluminum hydroxide from either aluminum nitrate or aluminum isopropoxide at 600°C (3) (catalyst 1). (2) Catalyst prepared by the thermal decomposition of alumina isopropoxide (360°C) followed by calcination at 600°C (catalyst 2). (3) Catalyst prepared by the slow hydrolysis of aluminum isopropoxide by prolonged (24-48 hr) exposure to humid atmosphere (relative humidity 50-70%) followed by heating initially at 120°C for 6 hr followed by heating at 600°C for 6 hr (catalyst 3). All the catalysts had surface area of  $200 \pm 20 \text{ m}^2/\text{g}$ . Further details of the preparation and characterization of catalysts 2 and 3 will be reported in another communication.

Experimental procedure for the catalytic reaction and analysis had already been reported (4).

Results of the reactions of benzyl alcohol over the three catalysts have been summarized in Table 1. It is clear that catalysts 2 and 3 are more active for alcohol conversion than catalyst 1. Catalyst 2 is selective for ether formation and catalyst 3 for disproportionation. However, it could be shown that the initially formed ether itself decomposed at increased contact times on all the catalysts. The results for catalyst 3 are represented in Fig. 1. It was further shown that dibenzyl ether itself underwent decomposition to benzaldehyde and toluene. Catalyst 3 was much more active for this reaction than catalyst 2 (Table 2). It could be seen from Table 1 that disproportionation increased and ether formation decreased with increase in reaction tempera-

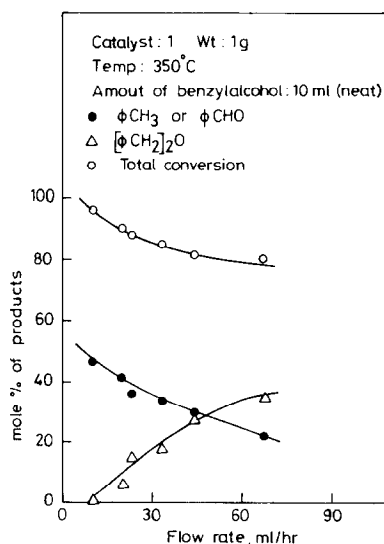


FIG. 1. Reaction of benzyl alcohol. Effect of flow rate on the distribution of products.

<sup>1</sup> For Part VII, see M. J. Andrews and C. N. Pillai, *Indian J. Chem.* 16B, 465 (1978).

TABLE 1  
Reaction of Benzyl Alcohol as a Function of Temperature

Alumina code No.	Temp. (°C)	Product distribution, mole% <sup>a</sup>				
		Toluene	Benzaldehyde	Diphenyl ether	Benzyl alcohol	Others <sup>b</sup>
1	300	16	16	37	30	1
	350	21	20	30	27	2
	390	30	30	21	16	3
2	300	6	5	73	14	2
	350	15	14	55	11	1
	390	26	25	39	9	1
3	300	26	25	32	16	1
	350	42	41	6	10	1
	390	43	43	5	7	2

*Note.* Weight of alumina: 1 g. Reactant: 10 ml of benzyl alcohol (neat). Flow rate: 20 ml/hr.

<sup>a</sup> The product distribution refers to composition of total product collected for the entire period of reaction.

<sup>b</sup> Diphenylmethane and 1,2-diphenylethane were identified. In addition, trace quantities of unidentified products were also present.

ture. These observations suggested that there were two routes for toluene and benzaldehyde, namely, disproportionation of benzyl alcohol and decomposition of dibenzyl ether. The molar equivalence of toluene and benzaldehyde, as well as the fact that no gaseous products were formed during the reaction, suggested that the disproportionation was a process involving the direct transfer of hydride from one surface benzyloxy species to a neighboring one, analogous to the mechanism already established

for the disproportionation of diphenylcarbinol over alumina (1).

It was found that when the reaction was done for a prolonged time on the same catalyst, there was a steady decrease in the activity of all the three catalysts. It was also found that along with the decrease in activity, there was an increase in ether formation and a decrease in disproportionation. The effect was qualitatively similar on all the catalysts, but was most spectacular on catalyst 3, which has been shown in Fig. 2.

TABLE 2  
Decomposition of Dibenzyl Ether

Alumina code No.	Temp. (°C)	Product distribution, mole% <sup>a</sup>			
		Toluene	Benzaldehyde	Dibenzyl ether	Others <sup>b</sup>
<sup>c</sup>	350	—	0.5	99	0.5
2	300	6	6	87	—
	350	13	14	72	1
	390	21	22	56	2
3	300	15	16	68	1
	350	38	39	20	3
	390	45	44	8	3

*Note.* Weight of alumina: 1 g. Flow rate: 20 ml/hr. Reactant: 10 ml of dibenzyl ether (neat).

<sup>a</sup> As per Table 1.

<sup>b</sup> As per Table 1.

<sup>c</sup> No catalyst was used. The reactor was packed with glass pieces.

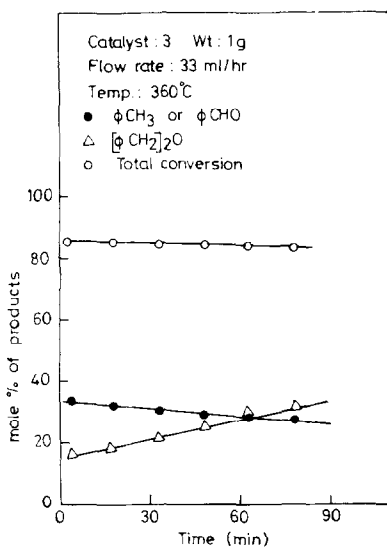


FIG. 2. Reaction of benzyl alcohol. Product distribution as a function of time.

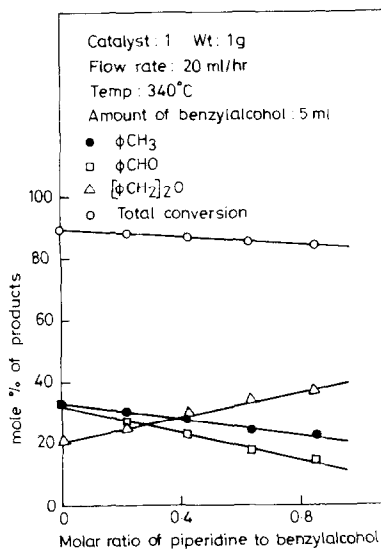


FIG. 3. Reaction of benzyl alcohol. Effect of piperidine on the distribution of products.

(The product distribution in the figure for any point,  $t$  minutes, on the  $x$  axis refers to the composition of total products collected between the  $(t - 2.5)$ th min to the  $(t + 2.5)$ th min.) The reduction in activity with reaction time was probably due to blocking of active sites by coke formation. It would appear that the sites responsible for disproportionation were selectively more deactivated by coke formation than the sites responsible for dehydration (ether formation). Discoloration of the catalyst indicating coke formation was maximum for catalyst 1, consistent with the observation that this was the catalyst which showed maximum loss of activity on usage.

Water formed during the reaction also seemed to inhibit the decomposition of ether. This was evident from the observation that the activity of catalyst 3 for the decomposition of dibenzyl ether to benzaldehyde and toluene (a reaction where water was not a product) was only marginally reduced with time. The decrease in the activity for benzyl alcohol conversion on this catalyst with time was also of the same order. However, the selectivity changed in favor of ether formation. This could only be

due to the selective poisoning of the disproportionation sites by the water formed in the reaction of benzyl alcohol.

Addition of increasing quantities of a base (piperidine, Fig. 3) also showed that the sites responsible for disproportionation were more easily poisoned than those for dehydration. As the concentration of piperidine increased the overall activity of catalyst 3 decreased, but the selectivity increased in favor of ether formation. The ratio benzaldehyde/toluene which was initially 1 decreased as the concentration of piperidine was increased. This was due to the secondary reactions between benzaldehyde and piperidine which are being separately investigated. Pyridine had a qualitatively similar, but much less pronounced effect.

These studies showed that alumina catalysts had two types of active sites with respect to the reaction of benzyl alcohol, namely, sites responsible for dehydration and those active for disproportionation. The latter are more readily deactivated by prolonged usage as well as by exposure to bases like piperidine, pyridine, and also by water. A highly selective catalyst could be

prepared which converted benzyl alcohol almost exclusively to benzaldehyde and toluene.

4. S. V. Kannan, and C. N. Pillai, *Indian J. Chem.* **8**, 1144 (1970).

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