JOURNAL OF CATALYSIS 53, 232–236 (1978)

Hydrogen Transfer Reactions

VI. Dependence of the Catalytic Activity of Alumina on Na^+ Content and Amine Poisoning[1]

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Received September 7, 1977; revised January 3, 1978

The dependence of Na^+ content on the activity of alumina with respect to the dehydration and dehydrogenation of alcohols, transfer hydrogenation of carbonyl compounds by alcohols, and disproportionation of diphenylcarbinol was studied. It was found that the activity for dehydration, hydrogen transfer, and disproportionation was related to the acidity of the catalyst. Doping with Na^+ ions and exposure to amines caused decrease in the activity for the above reactions, whereas the activity for the dehydrogenation of diphenylcarbinol increased on Na^+ doping.

INTRODUCTION

The reversible transfer hydrogenation of ketones and aldehydes by alcohols over Na^+-doped alumina at around 300°C has been reported (*1*). Similar reactions on alkali metal oxides (*2*) and on hydroxyapatite (*3*) have also been reported. Similarly disproportionation of diphenylcarbinol and transfer hydrogenolysis of the same carbinol by hydrogen donors (alcohols) over alumina have also been reported (*4*). Equations for illustrative examples of the above types of reactions are given below:

Transfer hydrogenation (*I*)

$$(C_6H_5)_2CO + (CH_3)_2CHOH \rightleftarrows (C_6H_5)_2CHOH + (CH_3)_2CO$$

Disproportionation (*II*)

$$2(C_6H_5)_2CHOH \rightarrow (C_6H_5)_2CO + (C_6H_5)_2CH_2 + H_2O$$

Transfer hydrogenolysis (*III*)

$$(C_6H_5)_2CHOH + (CH_3)_2CHOH \rightarrow (C_6H_5)_2CH_2 + (CH_3)_2CO + H_2O$$

The reactions over alumina are mechanistically significant in the sense that this catalyst which is normally not active for dehydrogenation readily causes the dehydrogenation of the donor alcohol when a hydrogen acceptor is present. Kibby and Hall (*3*) from their studies of the hydrogen transfer between alcohols and ketones have concluded that catalysts with maximum dehydrogenation activity were the best hydrogen transfer catalysts. According to Okamoto *et al.* (*2*) the basic property of the catalyst was responsible for hydrogen transfer activity.

Hydrogen transfer activity as illustrated

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[1] For Part V of this series, see Unni, M. P. K., Sreekumar, C., Hariharakrishnan, V. S., and Pillai, C. N., *J. Cat.* 53, 168 (1978).

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0021-9517/78/0532-0232$02.00/0

by reactions I, II, and III is exhibited by almost all oxides catalysts. A screening of a number of oxide catalysts (alumina, Na^+-doped alumina, nickel oxide, magnesium oxide, titanium dioxide, chromium oxide, nickel chromate, thorium oxide, zinc oxide, magnesium silicate) showed that they all catalyzed hydrogen transfer reactions at temperatures well below those at which the decomposition of the alcohols themselves (dehydration or dehydrogenation) took place (*5*). Though quantitative studies have not been completed the general conclusion is that catalysts of high Lewis acidity, especially alumina, are most active for hydrogen transfer. In the present paper a comparative study of alumina and Na^+-doped alumina catalysts for their dehydration, dehydrogenation, and hydrogen transfer activity using the transfer hydrogenation of benzaldehyde and cyclohexanone by isopropyl alcohol, the disproportionation and dehydrogenation of diphenylcarbinol, and the dehydration of isopropyl alcohol is reported. The effect of amines on catalytic activity has also been studied.

EXPERIMENTAL

Catalysts and Catalytic Reactions

Alumina and Na^+-doped alumina catalysts were prepared as reported earlier (*1*, *4*). Procedures for the catalytic reactions and product analysis have also been reported (*1*, *4*).

RESULTS AND DISCUSSION

Three samples of alumina containing 0, 0.95, and 2.2% by weight of Na^+ were used for the present study. The three catalysts had comparable surface areas and hence comparison of activities were made on a weight basis. Properties of the catalysts and their activities are listed in Table 1.

Dehydration Activity

It can be seen that the dehydration activity decreased with increase in Na^+ content. This poisoning effect of alkali metal ions on the dehydration activity of alumina is a well-known phenomenon (*8*). Though the incorporation of Na^+ does not

TABLE 1

Comparison of Three Alumina Catalysts

Sl number	Na^+ (wt%)	Surface area (m^2/g)[a]	Acidic and basic sites (mmol/g)[b]			Dehydration activity (% isopropyl alcohol reacted)[f]	Hydrogen transfer activity (% benzaldehyde reacted)[g]	Activity for diphenylcarbinol conversion[h]		
			Lewis acidity[c]	Bronsted acidity[d]	Basicity[e]			Total conversion (%)[h]	Dehydrogenation[i]	Disproportionation[j]
1	nil	175	0.1	0.04	0.9	40	68	100	nil	100
2	0.95	154	0.13	0.02	1.7	11	32	60	11	49
3	2.2	160	0.13	nil	2.0	nil	20	13	9	4

[a] By BET nitrogen adsorption method.

[b] From the Ph.D. Dissertation of S. Siddhan, Indian Institute of Technology, Madras, 1976.

[c] By butylamine adsorption; gives total Lewis acidity, weak as well as strong.

[d] Based on the ability of surface protons to liberate iodine from iodide–iodate mixture [see Ref. (*6*)].

[e] By trichloroacetic acid adsorption [see Ref. (*7*)].

[f] Isopropyl alcohol to propylene; weight of catalyst 2 g; flow rate 0.2 mol/hr; temperature 300°C.

[g] Reactants: benzaldehyde + isopropyl alcohol; 1:4 molar mixture; catalyst 2 g; flow rate 0.2 mol/hr; temperature 300°C. Material balance was obtained. The product from benzaldehyde was benzyl alcohol alone and the products from isopropyl alcohol were acetone and propylene. There was a 1:1 molar correspondance between the acetone formed and the benzaldehyde reacted in all three cases. Dehydration of isopropyl alcohol to propylene in mole% based on the isopropyl alcohol taken, corresponded to 2.5%, 1.5%, and nil on the three samples of alumina, respectively.

[h] From Ref. (*4*).

[i] Percentage of total conversion; estimated from the amount of hydrogen evolved after correcting for a slight thermal decomposition.

[j] Percentage of total conversion; estimated from the amount of diphenylmethane formed.

TABLE 2

The Effect of Amines on the Activity and Selectivity of Alumina[a]

S number	Base[b]	Product composition (mol%)					
		From cyclohexanone			From isopropyl alcohol		
		Cyclohexanone[c]	Cyclohexanol	Cyclohexene	Acetone	Isopropyl alcohol[c]	Propylene
1	None	11	27	62	89	9	2
2	Pyridine (1 ml)	42	23	35	58	41	1
3	Piperidine (1 ml)	61	28	11	39	61	0

[a] Reaction: transfer hydrogenation of cyclohexanone by isopropyl alcohol. Catalyst: alumina (undoped) (5 g). Reactant: 10 ml of a 1:1 molar mixture of cyclohexanone and isopropyl alcohol. Flow rate: 18 ml/hr. Temperature: 300°C.

[b] One milliliter of the base was added to 10 ml of the reaction mixture.

[c] Unreacted starting material.

alter the number of Lewis acid sites, it has been reported that the proportion of strong acid sites were reduced considerably and this has been pointed out as the cause for the reduction in dehydration activity (*8*). Treatment of the alumina with bases like pyridine or piperidine, which are believed to get adsorbed on Lewis acid sites, also decreased dehydration activity. This phenomenon is also well known and has been confirmed in the present study.

Hydrogen Transfer Activity

Hydrogen transfer activity also decreased with increase in Na^+ content but not as sharply as dehydration activity. The mechanism proposed by Ramana and Pillai (*9*) and elaborated in the preceding paper in this series for the transfer hydrogenation of ketones by alcohols visualized the adsorption of the ketone through the oxygen on a Lewis acid site, thereby polarizing the carbonyl group and making the carbonyl carbon atom a ready acceptor of hydride from an alcohol molecule dissociatively adsorbed on a neighboring site. Unlike dehydration of alcohol which requires the heterolysis of a C–O bond, this reaction requires only the polarization of a π bond and relatively weaker Lewis acid sites are sufficient.

The effect of pyridine and piperidine. While, from the foregoing, it is clear that undoped alumina was the most active for hydrogen transfer, when the aim was to reduce a carbonyl compound to the alcohol this catalyst was not the one of choice because dehydration of the alcohol took place in varying amounts. Alumina with 2.2% Na^+ had lower overall activity but high selectivity (almost complete absence of dehydration activity), and hence this was the catalyst of choice for preparative transfer hydrogenation. In this connection the effect of organic bases (pyridine and piperidine) on the activity and selectivity of alumina was investigated. The data are given in Table 2. It can be seen that on pure alumina the conversion was high, but the product cyclohexanol underwent dehydration to a large extent to cyclohexene. Mixing a small quantity of the weak base pyridine with the reaction mixture decreased the hydrogen transfer activity as well as dehydration activity to a certain extent while the stronger base, piperidine, inhibited both reactions significantly. With both bases the inhibiting effect on dehydration activity was greater than that on hydrogen transfer activity. This experiment further illustrated the role of the acid sites on hydrogen transfer activity.

It may be noted that while cyclohexanol underwent dehydration over unpoisoned alumina relatively readily, isopropyl alcohol was less prone to dehydration. This difference in the dehydration reactivity of cyclohexanol and isopropyl alcohol was verified by independent comparison of their rates of dehydration. This will form the subject matter of another paper.

In this connection it may be mentioned that the transfer hydrogenation of ketones by isopropyl alcohol followed by the dehydration of the product, that takes place over undoped alumina, is an effective one-step method for the conversion of certain ketones to olefins. Preparation of cyclohexene from cyclohexanone and styrene from acetophenone have been accomplished nearly quantitatively by this method.

Disproportionation Activity

The activity for the disproportionation of diphenylcarbinol also decreased with increase in Na^+ content (Table 1). This reaction involves the dissociation of the relatively polar C–O bond of diphenylcarbinol as the result of activation by a Lewis acid site, along with the transfer of a hydride from a neighboring dissociatively adsorbed diphenylcarbinol (*4*). Hence the dependence of the activity for this reaction also on the acidity of the catalyst was understandable. As expected, piperidine also suppressed the disproportionation activity.

Dehydrogenation Activity

Alumina is normally not a dehydrogenating catalyst. It has been reported that mild dehydrogenation activity in the decomposition of 2-propanol and 2-butanol was created by doping with Na^+ (*10–12*). Diphenylcarbinol was unique in that it underwent appreciable dehydrogenation to benzophenone over Na^+-doped alumina. Undoped alumina was inactive for the dehydrogenation of even this alcohol. The data in Table 1 were corrected for a slight thermal dehydrogenation of diphenylcarbinol that took place at 300°C (*4*). It is clear that the dehydrogenation activity of alumina is not related to the acidity unlike dehydration and hydrogen transfer activities.

CONCLUSION

As far as alumina and Na^+-doped aluminas were concerned, our conclusions were not in agreement with those of Kibby and Hall (*3*) or Okamoto *et al.* (*2*). The former authors had found a correlation between dehydrogenation activity and hydrogen transfer activity, and the latter authors found one between base strength and hydrogen transfer activity. Neither conclusion seemed to be valid for the system that we had studied. The conclusion from the present study was that for alumina catalysts, dehydration activity, hydrogen transfer activity, and activity for the disproportionation of diphenylcarbinol were related to acidity, but the activity for the dehydrogenation of diphenylcarbinol was dependent on some other factor. The mechanisms proposed by us for the first group of reactions elsewhere, and cited earlier in this paper, involving Lewis acid sites for the adsorption and activation of carbonyl compounds and neighboring pairs of Lewis acid and basic sites for the dissociative adsorption of alcohol appeared satisfactory.

ACKNOWLEDGMENTS

Grateful acknowledgment is made to the Council of Scientific and Industrial Research, New Delhi, and the National Bureau of Standards, Washington, D. C., for financial support.

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