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Elimination Reactions on Solid Acid Catalysts. I. A Comparison between Silica-alumina and Alumina Catalysts in the Dehydration of Ethanol by Means of the Poisoning Method

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Silica-alumina, alumina, and alumina-boria are solid acid catalysts useful in various acid-catalyzed reactions.[1] The correlations between the acidity and the catalytic activity have been established in some reactions;[2] however, no general conclusion has yet been obtained among all the acid-catalyzed reactions.

One of the present authors has reported previously that alumina showed a characteristic behavior in contrast with silica-alumina in the reaction with methylene chloride[3] and in dehydrochlorination reactions from chloroethanes,[4] although it had a very small activity in dealkylation reactions which were explained by the protonic acidity.[5,6]

Echigoya[7] discussed the differences between these two catalysts in some reactions and explained them in terms of the acid strength and the origins of their acid sites.

The dehydration of ethanol is one of the reactions which show a distinct difference between these two catalysts, and it has been investigated for many years.[7-9] Two kinds of mechanisms have been proposed; one is the carbonium-ion mechanism,[10] and the other, the alcohoxide mechanism.[11] Pines and Pillai[12] and Jain and Pillai[13] have shown the olefin and ether formations on alumina *via* a concerted mechanism by the poisoning method, using acidic and basic inhibitors.

In the present research, the reaction mechanism was investigated by the poisoning method, using pyridine and *n*-butylamine as the basic substances and acetic acid as an acidic substance in order to clarify the differences between silica-alumina and alumina in the dehydration of ethanol. Recently,

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[2] a) M. W. Tamele, *Discuss. Faraday Soc.*, **8**, 277 (1950); b) V. C. F. Holm, C. C. Bailey and A. Clark, *J. Phys. Chem.*, **63**, 129 (1959); c) K. Tanabe and T. Takeshita, "Acid-Base Catalysts," Sangyo Tosho (1965), p. 129.

[3] I. Mochida, J. Take, Y. Saito and Y. Yoneda, This Bulletin, **41**, 65 (1968).

[4] I. Mochida, J. Take, Y. Saito and Y. Yoneda, *J. Org. Chem.*, **32**, 3894 (1967).

[5] M. E. Johnson and J. S. Melic, *J. Phys. Chem.*, **65**, 1146 (1961).

[6] I. Mochida and Y. Yoneda, *J. Catal.*, **7**, 386 (1967).

[7] E. Echigoya, *Nippon Kagaku Zasshi*, **79**, 426, 430 (1958).

[8] M. E. Winfield, "Catalysis," Vol. 7, ed by P. H. Emmett, Reinhold Pub. Co., New York, N. Y. (1960), p. 93.

[9] H. Pines and J. Manassen, *Advan. Catal.*, **16**, 49 (1966).

[10] W. S. Bery and K. A. Krieger, *J. Amer. Chem. Soc.*, **71**, 3637 (1949).

[11] K. V. Topchieva, K. Yun Pin and I. V. Shirnova, *Advan. Catal.*, **9**, 799 (1957).

[12] H. Pines and C. N. Pillai, *J. Amer. Chem. Soc.*, **82**, 2401 (1960).

[13] J. R. Jain and C. N. Pillai, *J. Catal.*, **9**, 322 (1967).

Trambouze *et al.*[11] reported common concerted mechanisms for both alumina and silica-alumina by a similar poisoning method using tetracyanoethylene (TCNE) as the acidic substance. Very recently, Parera and Figoli[15] studied the differences between these two catalysts in the dehydration and methylation of methanol, and concluded that the active sites on silica-alumina were protonic-acid sites, whereas those on alumina were Lewis-acid sites.

Experimental

Reagents. Ethanol of a G. R. grade (Hayashi Junyaku Co.) and *n*-butylamine, pyridine, and acetic acid of an E. P. grade (Wako Junyaku Co.) were used without further purification. Isopropylbenzene was used after the removal of peroxide by an adsorption column of silica and alumina gels.[16]

TABLE 1. CATALYSTS

Abbreviation	Name	Surface area (m^2/g)	Composition	Remark
A	alumina	190		(a)
A-Na	alumina-NaOH	240	0.33 meq Na/g	(b)
AB	alumina-boria	390	10% B_2O_3	(c)
AB-Na	alumina-boria-NaOH	290	0.33 meq Na/g	(d)
SA	silica-alumina	550	13% Al_2O_3	(e)
SA-Na	silica-alumina-NaOH	500	0.42 meq Na/g	(f)

a) By precipitation of $Al(NO_3)_3$ with NH_4OH.
b) By impregnation of A with aq. NaOH.
c) By coprecipitation of $Al(NO_3)_3$ and H_3BO_3 with NH_4OH.
d) By impregnation of AB with aq. NaOH.
e) Nippon Cat, a cracking catalyst of the Shokubai Kasei Co.
f) By impregnation of SA with aq. NaOH.

Catalysts. The catalysts are listed in Table 1, together with some of their properties. They were all calcined at 550° for 8 hr in the atmosphere.

Apparatus and Procedures. An ordinary pulse technique with a hydrogen carrier gas was adopted for both reactions.[17] A 1-hr pretreatment of the catalyst was carried out in a hydrogen gas flow at 450°C. For dehydration, PEG-1500 (Gas Chro Kogyo Co.) was used in the analytical column (2 m, 70°C), and the reaction temperature was 350±2°C. The gas-chromatographic peaks of the products were broad on sodium-poisoned catalysts.[18] In this case, the products were once trapped by liquid nitrogen between the reactor and analytical column, and then they were simultaneously reevaporated for gas-chromatographic analysis. For deisopropylation, the analytical column contained 3 m of TCP (Gas Chro Kogyo Co.) and the reaction temperature was 440±2°C. The conversion was proportional to the reciprocal space velocity under a low conversion, so apparent rate constant, *k*, was obtained from the slope. To observe the effect of a base or acid addition, poisoning reagents were injected before the reaction. As basic inhibitors did not react with ethanol, a catalyst could then be used. In the case of acetic-acid poisoning, however, ethylacetate was formed on some catalysts, so the poisoning effect was measured over the catalysts poisoned for each observation.

Results

The Catalytic Activities of Silica-alumina, Alumina, and Their Related Catalysts in Dehydration and Deisopropylation Reactions. The catalytic activities for the dehydration of ethanol and for deisopropylation from isopropylbenzene are summarized in Table 2. The six catalysts studied may be classified into two groups: SA, SA-Na, and AB belong to one group, and A, A-Na, and AB-Na to the other group. The catalyst of

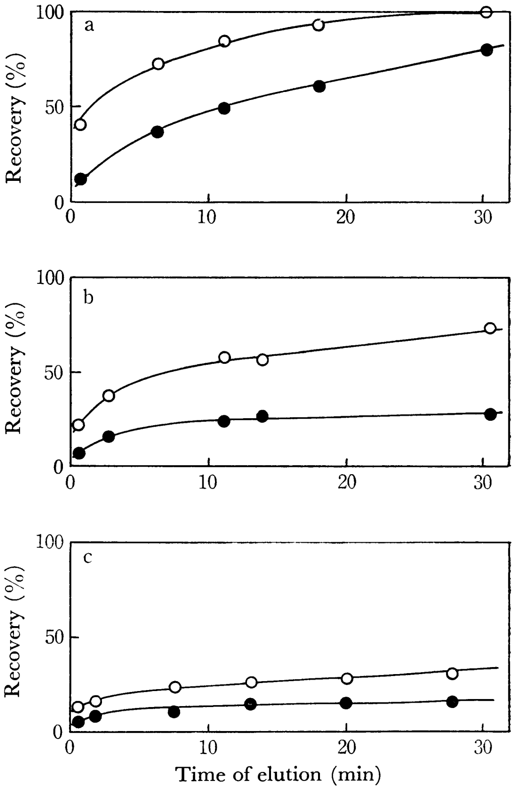

Fig. 1. Poisoning by *n*-butylamine for dehydration of ethanol at 350°C.
a, alumina; b, alumina-boria; c, silica-alumina
●, ethylene formation; ○, ether formation

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[14] F. F. Roca, L. De Mourgues and Y. Trambouze, *J. Catal.*, **14**, 107 (1969).

[15] J. M. Parera and N. S. Figoli, *ibid.*, **14**, 303 (1969).

[16] C. J. Prater and D. M. Nace, *Advan. Catal.*, **8**, 293 (1956).

[17] R. J. Kokes, H. Tobin and P. H. Emmett, *J. Amer. Chem. Soc.*, **77**, 5860 (1955).

[18] Y. Murakami, *Shokubai*, **5**, 192 (1963).

TABLE 2. RATES OF DEHYDRATION OF ETHANOL AND DEISOPROPYLATION OF ISOPROPYLBENZENE ON VARIOUS CATALYSTS

Catalyst	A	AB	SA	A-Na	AB-Na	SA-Na
Rate (m*l*/min·g) $(\times 10^3)$[a]						
of ethanol disappearance	4.2	3.0	4.5	1.2	1.0	0.89
of ethylene formation	2.1	1.9	3.0	0.60	0.54	0.53
of ether formation[b]	2.1	1.1	1.5	0.60	0.48	0.36
Ratio of formation rate[c]	1.0	1.7	2.0	1.0	1.1	1.5
Rate (m*l*/min·m²)	22	7.7	8.2	5.0	3.5	1.3
Rate (m*l*/min·m²·Al-atom)	22	8.5	69	—	—	—
Rate of deisopropylation from isopropylbenzene (m*l*/min·g)[d]	1.3×10^{-1}	6.6×10^{2}	2.4×10^{3}	*	2.6	9.6×10

a) Reaction temperature: 350°C, flow rate: 90 m*l*/min.
b) Ethanol base.
c) Ratio of ethylene/ether in ethanol base.
d) Reaction temperature: 440°C, flow rate: 90 m*l*/min.
* Too small to be measured.

the former group had a considerable activity for deisopropylation and its ethylene/ether ratio was larger than unity, whereas the catalyst of the latter group had a very small activity for deisopropylation and its ethylene/ether ratio was about unity. Sodium ions poisoned the catalysts of both groups in both reactions. It is interesting that AB-Na behaved much like A.

Poisoning by Nitrogen Bases. The addition of a nitrogen base to a catalyst before the reaction retarded the dehydration reaction to an extent according to the kind of catalyst and base. The activity recovered gradually as the elution by hydrogen proceeded. These phenomena may be explained by the adsorption and desorption of the nitrogen base on acidic sites. The cases with *n*-butylamine and pyridine are shown in Figs. 1 and 2 respectively. With more basic *n*-butylamine, the dehydration was retarded more and the recovery of the catalytic activity was slower. The catalyst with a considerable activity for deisopropylation, the first group, was poisoned more severely, but A-Na or AB-Na suffered no effect. Generally speaking, the nitrogen base poisoned the ethylene formation more than the ether formation. This selective poisoning was most distinct with pyridine as an organic base and AB as a catalyst, when only the ethylene formation was retarded. Moreover, more poisoning of the sodium ion against ethylene formations on silica-alumina and alumina has been reported.[7,19]

Poisoning by Acetic Acid. The effect of an acid addition on dehydration was studied for SA, AB, and A from a viewpoint similar to that reported by Pines and Pillai[12] and by Jain and Pillai.[13] The results are shown in Fig. 3. Acetic acid also poisoned the ethylene formation more. Speaking of catalysts, they were poisoned in this order: A> AB>SA, which was just the reverse of that in the nitrogen-base poisoning. In the cases of SA and AB, the ester was found in the first pulse, but it disappeared in the second and following pulses, when the poisoning for ether formation also disappeared. On A, the ester was not found at all,

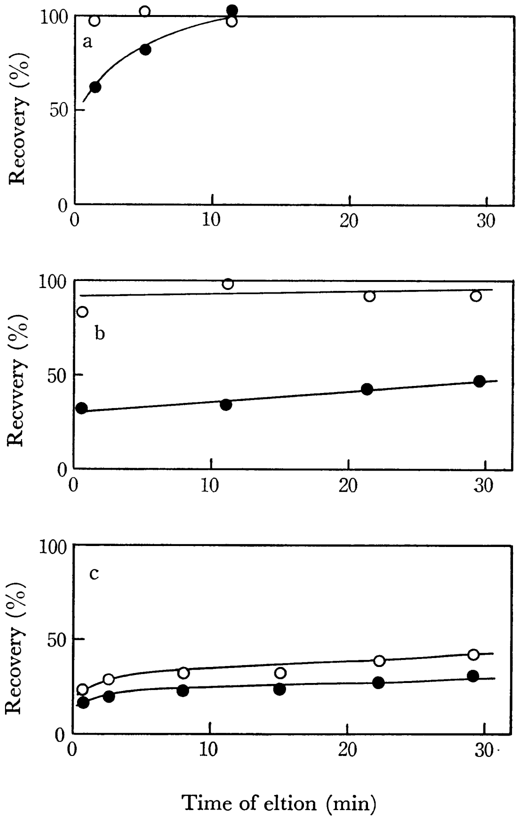

Fig. 2. Posioning by pyridine for dehydration of ethanol at 350°C.

a, alumina; b, alumina-boria; c, silica-alumina
●, ethylene formation; ○, ether formation

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[19] J. Take and Y. Yoneda, *ibid.*, **7**, 317 (1965).

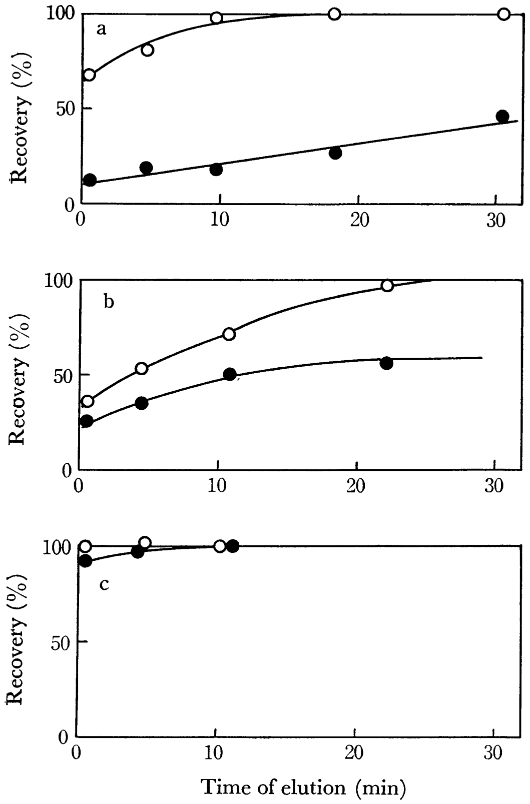

Fig. 3. Posioning by acetic acid for dehydration of ethanol at 350°C.
a, alumina; b, alumina-boria; c, silica-alumina
●, ethylene formation; ○, ether formation

although acetic acid might be adsorbed. All sodium-poisoned catalysts except SA-Na were poisoned more severely than their original catalysts.

Discussion

As has been described in the results section, the catalysts studied were classified into two groups. As for the silica-alumina group, on which a considerable deisopropylation occurred, the dehydration may take place on the strong acid sites, as is to be expected from the fact that deisopropylation proceeded on such sites.[5-7] The decrease in activity which occurred upon the addition of a sodium ion or organic bases supports the above mechanism. The active sites may not include the basic site, which is different from the sites on the alumina group, because acetic acid had little effect on dehydration, although the phenomena became complex about AB, where parts unperturbed by the presence of boria were left. Recently, Trambouze *et al.*[14] has reported that the active sites for dehydration on silica-alumina contained basic points as well as acidic points; however, the present authors observed that TCNE poisoned the deisopropylation as well. Therefore, it is possible that the adsorption of bulky TCNE on a weak basic site retarded the reaction on an acid site. The same situation may occur in dehydration. The results on alumina suggest that the ethylene formation proceeds through a concerted mechanism on an acidic site and a basic site[9,12] including an ethoxide intermediate.[20,21] The adsorption of acetic acid on basic sites may be verified by the fact that acetic acid poisoned A-Na more severely than A. Echigoya[7] defined the Lewis acid for alumina and the Brönsted acid for silica-alumina and proposed hydrated Lewis acids as active sites on alumina for dehydration. However, the aluminum ion, which can accept ethanol in an ethoxide, is more probable as the active site, although the former part of Echigoya's definition may be true. Parera and Figoli[15] reached a similar conclusion in the reaction of methanol. These differences in the mechanism and the active site might bring about the distinct difference in the dehydrations on silica-alumina and alumina.

The esterification of ethanol with acetic acid on silica-alumina was much faster than on alumina, although the esterification may proceed on weaker acid sites than dehydration. Here an interesting difference was observed between two catalysts. The results of our investigation of this reaction in connection with dehydration will be published later.

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20) H. Arai, J. Take, Y. Saito and Y. Yoneda, *J. Catal.*, **9**, 146 (1967).

21) H. Arai, Y. Saito and Y. Yoneda, This Bulletin, **40**, 731 (1967).