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Elimination Reactions on Solid Acid Catalysts

III. Dehydration of Ethanol on Metal Sulfates

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Dehydration of ethanol over 10 metal sulfates has been studied at 300° with the pulse technique to examine which properties of the solid catalyst influence the activity and selectivity of ethylene/ethyl ether formation in this dehydration. The activity and the selectivity varied from one metal sulfate to another. The intramolecular/intermolecular selectivities in dehydration of ethanol, *n*-propanol, and the ethanol–acetic acid system on the metal sulfate were linearly correlated with each other; however, they could not be related to an explicit property of the catalyst. The geometry, as well as the acidity of the active site on the solid surface, was found to be important in this reaction, as shown by studies of *n*-butylamine poisoning. To diminish the importance of geometry among the catalysts, metal sulfates were also supported on silica gel, where the electronegativity of the metal ion was found to be a good parameter for a description of the activity and selectivity. Effects of calcination temperatures on the activity and selectivity of both unsupported and supported catalysts were investigated. The nature of the active site was discussed.

INTRODUCTION

The dehydration of ethanol is an acid-catalyzed reaction which has been investigated for many years (*1*). Studies of kinetics, with discussion based on LFER, (linear free energy relationships), detection of reaction intermediates by IR, poisoning experiments using acidic and basic substances, and investigations with the tracer technique have all been reported (*1*, *2*). As for ethylene/ethyl ether selectivity, Take and Yoneda (*3*) discussed the effects of sodium poisoning, using silica–alumina catalysts. The authors discerned the active sites for these products by the poisoning method (*2a*). Bryant and Kranich (*4*) reported that the selectivity on zeolite catalysts was influenced principally by their pore sizes. Arai *et al.* (*2b*) claimed the importance of the alumina content of silica–alumina, on which alcoxide was formed. However, the factors of the solid catalyst which determine the selectivity of this dehydration have not yet been established. It was thought to be interesting to correlate the acidities of a series of solid catalysts with their selectivities.

A series of metal sulfates form a typical group of solid acid catalysts, and their activities have been studied extensively (*5*, *6*). In the present work, the role of catalyst acidity in the dehydration of ethanol has been investigated systematically among such a series of metal sulfates, and in this connection we may note that the electronegativity (χ_i) has been reported as a useful parameter for a description of activity and selectivity in acid-catalyzed reactions (*7*, *8*).

EXPERIMENTAL METHODS

Ethanol of G. R. grade (Hayashi Junyaku Co.) and *n*-butylamine of E. P.

grade (Wako Junyaku Co.) were used without further purification.

Metal sulfates were of G. R. grade (Hayashi Junyaku Co.). The supported metal sulfates were obtained by impregnating silica gel (Wako Junyaku Co.) with the prescribed amount of metal sulfates, and then drying at 120° in the atmosphere. The reaction rates and selectivities were measured at 300° by the pulse technique with a helium carrier. The catalysts were pretreated in the carrier flow for 3 hr at a temperature of 300–450°. The catalytic activity decreased gradually with successive pulses, so the activities and selectivities were calculated from the first pulse conversion. It is well known that the ethylene/ethyl ether ratio depends on the partial pressure of ethanol, so the injection and evaporation of the reactant were carried out with precautions to give a similar pulse shape in each run. The activity and selectivity thus obtained were reproduced within 10%. The pulse shape was strictly a triangle, but the appropriate reactangle may be permitted for the first approximation.

RESULTS AND DISCUSSION

Dehydration of ethanol on metal sulfates. Ethanol was converted into ethylene and ethyl ether on metal sulfates calcined at 300°. The contact time dependence of product formation is shown in Fig. 1; ethylene/ethyl ether ratios were constant below 20% conversion and above this value, ethylene formation was accelerated and ethyl ether formation was depressed. This profile may mean that these processes were competing at low conversions, but the successive dehydration of ethyl ether took place to a considerable degree at high conversions. This reaction scheme seems common on many solid acid catalysts (*1*). The ethylene/ethyl ether ratio should be studied at low conversions to discuss this selectivity in connection with the nature of the catalysts. The proportional constant of the conversion below 20% with the contact time can be considered as the rate by a differential reactor.

The selectivities are summarized in Table 1. The fact that they vary so much, depending on the metal ion, indicates that the dehydration on metal sulfates is suitable for a discussion of which properties of the catalyst determine the activity and selectivity. The activity and selectivity defined here are based on a rate which contains the adsorption constant of the reactant besides the rate constant and the

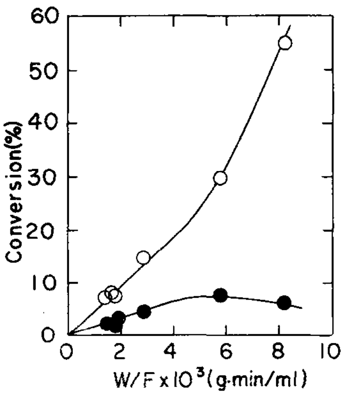

FIG. 1. Ethylene and ethyl ether formations at 300° vs the contact time: catalyst, $MgSO_4$ calcined at 300°; ○, ethylene; ●, ethyl ether.

TABLE 1
DEHYDRATION OF ETHANOL ON METAL SULFATES AT 300°

Sulfate	Dehydration		χ_i[a]	pK_a[b]
	Activity[c]	Selectivity[d]		
Ca(II)	1.3	50	5.0	12.6
Mg(II)	4.6×10	3.4	6.0	11.4
Ni(II)	1.8×10	3.0	9.0	10.6
Cr(III)	1.1×10	2.5	11.2	3.8
Mn(II)	1.2×10	2.0	7.5	10.6
Al(III)	6.7×10^2	1.9	10.5	5.1
Fe(III)	2.1×10	1.4	12.6	2.2
Zn(II)	4.7	1.3	8.0	8.8
Co(II)	6.0×10	1.1	9.0	8.9
Cu(II)	7.2×10	0.66	9.5	6.8

[a] Electronegativity, values from Ref. (*7*).

[b] Acid ionization constants for aquo ions at 25° from F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions." p. 32. Wiley, New York, 1967.

[c] (ml/g min).

[d] Ethylene/ethyl ether ratio on an ethanol basis.

partial pressure of the reactant. The rate and adsorption constants should be independently related with the properties of the catalyst, and should preferably be separated for discussion of the function of the catalyst. For a first-step approach, however, it is sufficient to seek relations between the rate observed under identical conditions, as this will give clues to understand the catalysis.

Propylene/n-propyl ether ratio from n-propanol, and ethylene/ethyl acetate from the ethanol–acetic acid system were compared with ethylene/ethyl ether from ethanol on seven metal sulfates. The selectivities of these reactions may be common in terms of the intermolecular/intramolecular ones. In fact, linear relations were observed among these selectivities, as shown in Fig. 2. The propylene/isopropyl ether ratio from isopropanol on cupric sulfate was 200, and the ether could not be detected on magnesium sulfate. Comparing n-propanol with isopropanol, the free energies of the reactions seemed to have little effect on the product distribution, because propylene/isopropyl ether is expected to be nearly equal to propylene/n-propyl ether in the equilibrium composition.* Incidentally, the intermolecular esterification was faster than the intramolecular dehydration in the presence of acetic acid. These intramolecular/intermolecular selectivities mean that the reactivity of the reactant influenced this selectivity to a considerable degree.

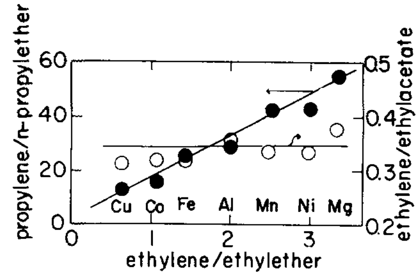

FIG. 2. Correlations among intermolecular and intramolecular dehydrations over metal sulfates calcined at 300°: ○, n-propanol; ●, ethanol–acetic acid system.

The δ_G LFER (*9*) in Fig. 2 suggests that there may be common factors determining these selectivities on each sulfate. One of the properties of the catalyst which contributes to the reactivity of the adsorbed alcohol may be the acidity. The latter is well estimated from the electronegativity of the metal ion (*7*, *8*), so the comparison between this value and the activity and selectivity is shown in Table 1, where the values of electronegativity were those reported by Tanaka and Ozaki (*7*). No simple relation could be found. The surface areas of metal sulfates calcined at 300° were estimated to differ considerably from one metal sulfate to another, but an accurate measurement was not obtained because of their small values (below 10 m^2/g). The distance between two adsorbed molecules, as well as their reactivities, should affect the selectivity, so a failure to find a correlation between the electronegativity and the selectivity may not be surprising.

Effect of n-butylamine addition before the reaction. The addition of n-butylamine before the reaction retarded the dehydration on metal sulfates, as shown in Fig. 3. Elution by the carrier gas gradually recovered the catalytic activity. The ethylene/ethyl ether ratio on the metal sulfate poisoned by n-butylamine was generally larger than that of the unpoisoned system, as shown in Table 2. On silica–alumina or alumina, the selectivity ratio was reduced by the poisoning (*2a*, *c*). The latter situation was attributed to the stronger acid site for the preferable ethylene formation being more poisoned, whereas the weaker site for the ethyl ether formation was re-

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* The free energies (kcal/mole) of the reactions at 600°K are as follows:

	n-Propanol	Isopropanol
Alcohol → propylene + H_2O	−10.33	−8.76
2x Alcohol → ether + H_2O	0.37	1.91
Difference	−10.70	−10.67

These data are taken from D. R. Stull, E. F. Westrum, and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds." pp. 229, 313, 416, 424. Wiley, New York, 1968.

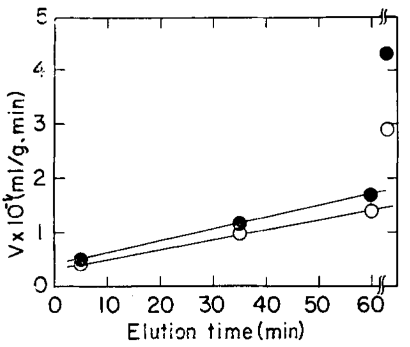

FIG. 3. Poisoning of n-butylamine against the dehydration of ethanol on cupric sulfate calcined at 300°: ○, ethylene formation; ●, ethyl ether formation.

covered more rapidly. If the acid sites are uniform or poisoned without discrimination of the acid strength, the intermolecular reaction may be retarded geometrically by an intervention of n-butylamine between two adsorbed alcohol molecules. When the mixture of n-butylamine and the reactant was injected, the ethylene/ethyl ether ratio became larger even on silica–alumina (*2a*), probably because the amine was interacting with acid sites in a random fashion during the reaction. Thus, the geometrical distribution of the active sites plays an important role for the selectivity determination, and the sites available for the dehydration may be more uniform on the metal sulfate than on silica–alumina.

TABLE 2
EFFECT OF n-BUTYLAMINE POISONING ON ETHYLENE/ETHYL ETHER RATIO OVER METAL SULFATES

Catalyst	Ethylene/ethyl ether[a] Without poisoning	Ethylene/ethyl ether[a] With poisoning[c]
$MgSO_4$	3.4	15.6
$NiSO_4$	3.0	10.6
$Al_2(SO_4)_3$	1.9	3.4
$CoSO_4$	1.1	4.6
$CuSO_4$	0.66	0.9
$CuSO_4$–SiO_2	5.0	7.8
SiO_2–Al_2O_3	2.0[b]	1.0[b]

[a] On an ethanol basis.
[b] At 350°.
[c] One hr after addition of 2 μl of n-butylamine.

Silica gel-supported catalysts. Misono *et al.* (*8*) succeeded in correlating the catalytic activity and the selectivity of metal sulfates for n-butene isomerization with the electronegativity of the metal ion by supporting on silica gel. By this method, the differences of the geometrical factor among the metal sulfates may be reduced because the surface area of the supporting silica gel is constant, and the activity of silica gel can be neglected in comparison with that of the supported metal sulfate.

The influence of the concentration of supported metal sulfate on the activity and the selectivity is shown in Table 3.

TABLE 3
EFFECT OF CONCENTRATION OF METAL SULFATE IN SILICA GEL-SUPPORTED CATALYST ON DEHYDRATION OF ETHANOL

Metal sulfate	Conc (meq/ g-SiO_2)	Activity ($\times 10^2$; ml/g min)	Ethylene/ethyl ether on an ethanol basis
$CuSO_4$	0.1	1.1	7.4
	0.4	4.6	5.2
	1.0	5.6	4.7
$NiSO_4$	0.2	1.1	4.5
	0.4	2.2	3.2

At low concentrations, the activity was proportional to the amount of the metal sulfate. The ethylene/ethyl ether selectivity was increased by the n-butylamine poisoning on $CuSO_4$–SiO_2 as shown in Table 2. Thus, the distribution of the active sites may be uniform, although the acid strength was increased (*8*). The selectivity was larger at small concentrations, where the distance between adsorbed molecules was increased, so we conclude that the intermolecular reaction may be difficult.

The contribution of the metal ion to the selectivity can be examined under the same geometrical conditions by comparing catalysts with the same concentration of metal sulfate. The activities and selectivities on the catalysts of 0.4 meq of metal sulfate/g-SiO_2 are correlated with electronegativities of metal ions in Fig. 4. A good linear relation was obtained for logarithmic rates, where the total activity for the dehydration was taken because a common intermediate (*2b*) was presumed for both products and thus the catalytic activity may be represented by this quantity. This dehydration was found to belong to a reaction group containing hydration of propylene, polymerization of acetaldehyde, and isomerization of butenes which have been correlated with the electronegativity of the metal ion (*7*, *8*). Shirasaki *et al.* (*10*) reported such a relation in the dehydration of isopropanol on metal ion exchanged silica–alumina catalysts. The relations may be explained on the grounds that the reactivity of the adsorbed reactant is accelerated by the high acidity produced by metal ions of large electronegativity, although which active sites, Brønsted or Lewis, serve in these reactions remains in question.

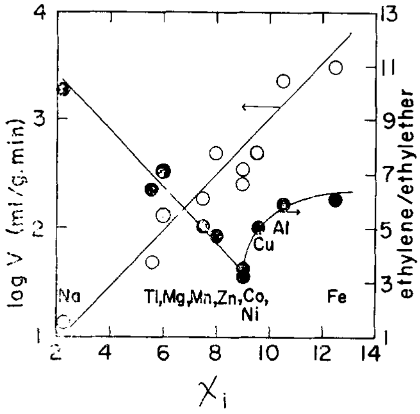

FIG. 4. Correlations of electronegativity of metal ion with the catalytic activity and selectivity of the metal sulfate supported on silica gel: ○, activity; ●, ethylene/ethyl ether ratio on an ethanol basis.

The selectivity of ethylene/ethyl ether varied in an antivolcano shape with the minimum at nickel and cobaltous ions. The adsorbed alcohol of high reactivity may direct to the intramolecular reaction because it is too reactive to migrate over the catalyst surface without being converted into the final product of the intramolecular reaction. It is well known in the homogeneous reaction that ethylene is formed in more severe conditions than ether (*11*). In the case of too small acidity, the surface concentration of the adsorbed alcohol may be too small, resulting in a disadvantage for the intermolecular reaction. Hence medium acidity is most suitable for the intermolecular reaction.

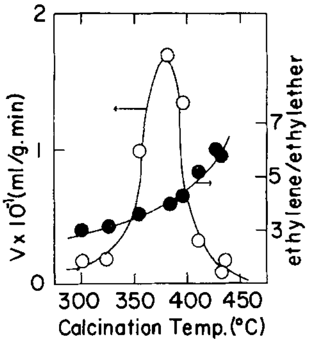

FIG. 5. The effect of calcination temperature on the catalytic activity and selectivity of nickel sulfate: ○, activity; ●, ethylene/ethyl ether ratio on an ethanol basis.

Effect of calcination temperature. The activity of the metal sulfate was reportedly influenced by the calcination temperature (*5*, *12*). The cases for nickel and cupric sulfates are shown in Figs. 5 and 6, respectively. The water produced has little effect because the reaction rate was calculated from the first pulse conversion. Nickel sulfate showed a distinct maximum activity at 370° as with the dehydration of *n*-butanol and other reactions (*5*, *8*, *13*).

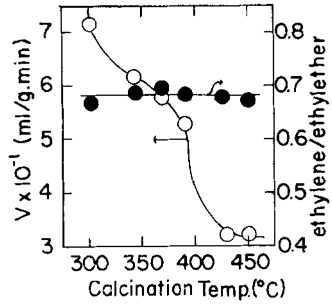

FIG. 6. The effects of calcination temperature on the catalytic activity and selectivity of cupric sulfate: ○, activity; ●, ethylene/ethyl ether ratio on an ethanol basis.

The activities of other sulfates such as cupric, magnesium, cobaltous, and aluminum sulfates above 300° decreased monotonically with increased calcination temperature as in butene isomerization (*8*). Butadiene and *n*-butenes were produced in a considerable amount on nickel sulfate calcined above 400°. They were not observed on cupric sulfate, where only acetaldehyde was detected. This Lebedev reaction (*14*) is interesting as another intermolecular reaction.

Monotonic decrease of the activity was also observed on supported nickel sulfate, as shown in Fig. 7. The surface area of the supported catalyst should vary little under these conditions, so the activity seems to depend not on the strain of the crystal as ascribed for the unsupported catalyst (*12*), but simply on the amount of protons. At 350°, the main part of the active sites may be transformed from Brønsted type to Lewis type, and the activity of the latter may be smaller than that of the former.

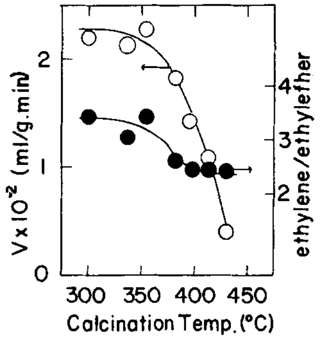

FIG. 7. The effect of calcination temperature on the catalytic activity and selectivity of nickel sulfate supported on silica gel (0.4 meq/g-SiO_2): ○, activity; ●, ethylene/ethyl ether ratio on an ethanol basis.

The selectivities on most metal sulfates increased with increased calcination temperature, as shown in Fig. 5, but not for cupric and aluminum sulfate, as shown in Fig. 6. The change of selectivity should be connected with the changes of surface concentration and activity of the active site. Surface area was, in fact, varied considerably (*12, 15*), so the surface state may be changed as well. However, these situations seem too complex to be discussed.

A change of selectivity was observed at 350° on the supported nickel sulfate, as shown in Fig. 7. The phenomenon may be understood by the same explanation as adopted for the activity variation, because both changes occurred at the same temperature.

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