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Acidity of Hydrated Sulfates Revealed by the Enolization of Acetone

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In previous papers,[1,2] an equation for electronegativity of the metal ions was derived by extending Mulliken's electronegativity concept[3] as follows.

$$X_i = \frac{\partial \sum I_j}{\partial Z} = (1+2Z)X_0 \qquad (1)$$

where I_j, is the j-th ionization potential, Z is the valence number of the ion and X_0 is the electronegativity of the metal ($Z=0$) with the Pauling scale. The electronegativity of the metal ions given by Eq. (1) has been found to be a good parameter of the acidity of the metal ions;[1,2,3] the ionization equilibrium (pK_a), $M(H_2O)_m^{\alpha+}+H_2O \rightleftharpoons H_3O^+ + M(H_2O)_{m-1}(OH)^{\alpha-1}$, being represented by

$$pK_a = 20\left(1-\frac{X_i}{14}\right) \qquad (2)$$

and the zero point of charge (ZPC) of the immersed oxides in water being formulated as follows.

$$\mathrm{ZPC} = 16.8\left(1-\frac{X_i}{22}\right) \qquad (3)$$

The catalytic activities of the sulfates for reactions such as hydration of propylene, dehydration of formic acid and polymerization of acetaldehyde are well correlated with the electronegativity of the metal ions.[2,4]

In this paper, the enolization of acetone is adopted as a monitor of the acidity of the hydrated sulfates, which has been found to be subject to general acid catalysis in homogeneous catalysis.

Experimental

A flow system with nitrogen carrier gas was employed. The carrier gas was bubbled through evaporating chambers of acetone (spectro grade) and of D_2O (99.8%), the total flow rate being kept at 72 ml/min for all experiments. The temperature of the acetone chamber was kept at 9.5 °C, and the concentration of acetone vaporized into the carrier was 1.3_1 vol% as determined by gas chromatographic analysis. The content of D_2O in the carrier gas was controlled by adjusting the temperature of the D_2O chamber. The concentration of D_2O was previously calibrated by measuring the weight increase of silica gel adsorbent when the carrier gas was passed through the silica-gel bed for a given time. All experiments other than those for the determination of D_2O pressure dependence were carried out with a constant D_2O concentration of 1.6_5 vol%.

The sulfates of 0.13 g (Fe^{3+}, Al^{3+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, and Mg^{2+}) were used without any supporting materials by treating at 140 °C for 4—5 hr in air and ground. The carrier gas containing D_2O and acetone was made to flow over the catalyst bed for about 30 min to reach a steady state, and then an acetone sample for the mass spectrometric analysis was collected at the outlet of the reactor by a liquid nitrogen trap. Analysis was carried out by using parent peaks at 10 eV with the correction of the natural abundance of ^{13}C.

The surface areas of the sulfates were measured by the BET method after they had been heated at 140 °C for 3 hr in air and evacuated at room temperature. The contact time of the reactant through the catalyst bed was estimated from the retention volume of the sulfates packed in a gas chromatographic column. The relative catalytic activity k_r was obtained by normalizing the reaction rate with surface area S and contact time t for each of the sulfates; $k_r = -2.303/St \cdot \log(d_0/d_0^0)$, in which d_0^0 and d_0 are the fraction of acetone-d_0 of the initial and of the trapped samples.

The isotope effect on the enolization of acetone was studied with acetone-d_6(99.5%) and H_2O over a nickel sulfate under the same experimental conditions as mentioned above.

Results and Discussion

A typical deuterium distribution of acetone obtained over a nickel sulfate is given in Table 1, the deuterium distribution obtained on the other sulfates being similar to that on the nickel sulfate. The deuterium distribution reveals that the hydrogen exchange of acetone proceeds consecutively, *viz.*, the desorption and adsorption of acetone are rapid as compared with the exchange reaction rate. When the deuteration of acetone proceeds with the consecutive exchange of d_0 to d_1, d_1 to d_2, *etc.*, the values of d_1 can be calculated by assuming that the second step ($d_1 \rightarrow d_2$) is 5/6 of the first step ($d_0 \rightarrow d_1$); $d_1 = (e^{-k_1 t} - e^{-k_0 t})/(1-k_1/k_0)$, where $k_1/k_0 = 5/6$. However, the calculated values are larger than the experimental values (Table 1) by factors of 1.2 at 98 and 110 °C, at 121 °C and 1.5 at 130 °C. The fact that the experimental value of d_1 is smaller than the calculated value may be due to partly occurring multiple exchange of adsorbed acetone.

The effect of D_2O pressures on the deuteration of acetone studied over nickel sulfate by changing D_2O

Table 1. Deuterium distribution in acetone over $NiSO_4$

Reaction temp. (°C)	d_0	d_1	d_2	d_3	d_4	d_5	d_6
98	95.6	3.9	0.5	—	—	—	—
110	93.2	5.4	1.4	—	—	—	—
121	87.6	9.1	2.6	0.7	—	—	—
130	82.9	10.2	4.4	1.8	0.7	—	—

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[1] K. Tanaka, A. Ozaki, and K. Tamaru, *Shokubai*, **6**, 22 (1964).

[2] K. Tanaka and A. Ozaki, *J. Catal.*, **8**, 1 (1967).

[3] R. P. Iczkowski and J. L. Margrave, *J. Amer. Chem. Soc.*, **83**, 3547 (1961).

[4] K. Tanaka and A. Ozaki, This Bulletin, **41**, 2813 (1968).

pressures from 3.2 to 14.7 mmHg is shown in Fig. 1.

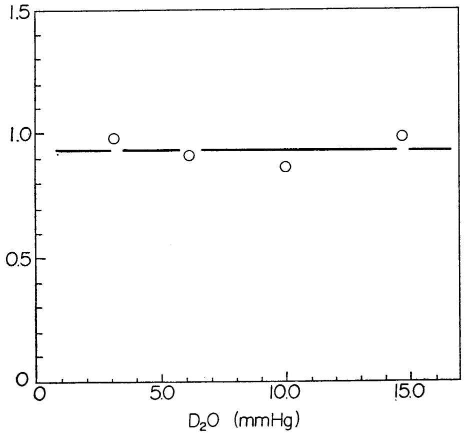

Fig. 1. D_2O pressure effect on the deuteration of acetone over a nickel sulfate at 98 °C.

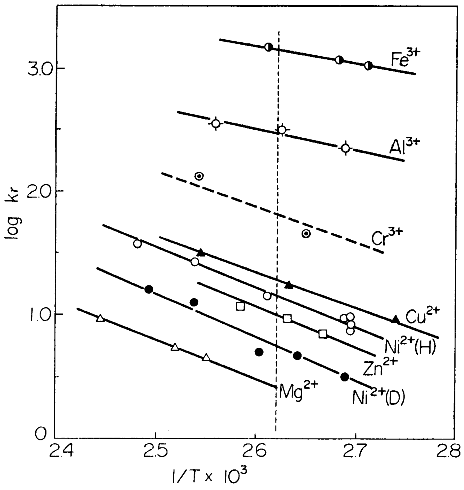

Fig. 2. Relative catalytic activities of the sulfates. Ni(D) is the reaction of acetone-d_6 with H_2O.

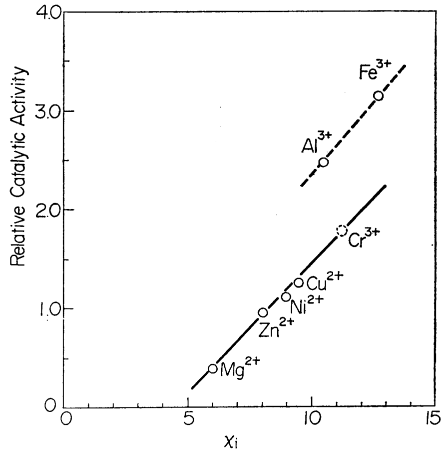

Fig. 3. Relation between the catalytic activity of the sulfate and the electronegativity of the metal ion.

It is seen that D_2O pressure has little influence on the hydrogen exchange rate between acetone and D_2O. This shows that the surface of the sulfate is covered with D_2O during exchange reaction, which is consistent by comparing with the temperature of the monohydrated nickel sulfate formation, 150 °C.[5]

It has been established that the enolization of acetone is subject to general acid catalysis in solutions with the rate-determining step of deprotonation of α-C–H.[7] If the enolization of acetone over the sulfates occurs with the same slow step, a large kinetic isotope effect is expected when α-C–H is replaced by α-C–D. For the sake of confirmation, the exchange reaction between acetone-d_6 and H_2O was carried out on a nickel sulfate under the same conditions; a flowr ate of 72 ml/min of carrier gas containing 1.3_1 vol.% of acetone-d_6 and 1.6_5 vol.% of H_2O. The exchange reaction between ordinary acetone and D_2O, denoted by Ni(H) in Fig. 2, is much faster than that between acetone-d_6 and H_2O, Ni(D), with $k_H/k_D \simeq 2.7$ at 100 °C. This supports a rapid prototation forming $(CH_3)_2COD^+$ followed by a slow deprotonation of α-C–H. With the increase of the acidity of H_2O or D_2O hydrated over the sulfates, the pre-equilibrium shifts to the protonated form causing an increase in the exchange reaction rate.

The deuteration of acetone carried out over the various sulfates is shown in Fig. 2, in which the ordinate is the logarithm of the relative catalytic activity (k_r). The activity sequence of the sulfates is in the order of $Fe^{3+} > Al^{3+} > Cr^{3+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Mg^{2+}$.

It has been shown that the proton activity of water hydrated over the oxides as well as the water hydrated around the metal ions is well correlated with the parameter X_i in the form of Eqs. (2) and (3). These relations reveal that the proton activity of the water hydrated over the sulfates may also be expressed by a similar equation of logarithmic form. Figure 3 shows the relation between the catalytic activities of the sulfates at a given temperature, indicated by a dotted line in Fig. 2, and the electronegativity of the metal ion. It is seen that the logarithm of the catalytic activities increases linearly with X_i as expected, but the activities are separated in the two groups, divalent sulfates and trivalent sulfates, in which the values for Cr^{3+} are much obscure because of its small surface area and the low apparent activity. It should be noted that the apparent activation energies over the trivalent sulfates are approximately half of those over the divalent sulfates.

It may be concluded that the acidity of the hydrated sulfates is well expressed by using the electronegativity of the metal ions on which water hydrates or adsorbs. The acidity discussed here apparently differs from that observed by Tanabe and his co-workers,[6] which strongly depends on the dehydration temperatures of the sulfates attaining maximum acidity and catalytic activity just before reaching the anhydrous state.

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[6] T. Takeshita, R. Ohnishi, T. Matsui, and K. Tanabe, *J. Phys. Chem.*, **69**, 4077 (1965). K. Tanabe and T. Takeshita, *Advan. Catal.*, **17**, 315 (1967).

[7] *Cf.* E. S. Gould, "Mechanism and Structure in Organic Chemistry," p. 372, Henry Hole and Co. N. Y.