The Catalytic Activity of Sulfate in the Decomposition of Formic Acid

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In our previous papers[1] it has been shown that the acidity of the aquo-ion given by the hydrolysis equilibrium constant (pK_a) can be formulated with a generalized electronegativity of the metal ion (X_i) as follows;

$$\mathrm{p}K_a = 20\left(1-\frac{X_i}{14}\right)$$

$$X_i = (1+2Z)X_0$$

where X_0 is the electronegativity of the neutral atom ($Z=0$) given by Pauling and where Z is the charge of the ion. This parameter can be successfully applied to solid surfaces; the acid-base properties of the hydrated oxide surface designated by Zero Point of Charge are expressed by the following equation;

$$\text{Zero Point of Charge} = 16.8(1-22/X_i)$$

and the catalytic activity of sulfate in the hydration reaction of propylene and the polymerization of acetaldehyde increase with the acidity parameter, X_i.

It is known that the decomposition of formic acid involves two reactions, dehydration and dehydrogenation, and that the dehydration reaction is commonly promoted by acid. In this experiment, the decomposition of formic acid has been adopted as a test reaction in order to demonstrate a general trend of the catalytic activity of the sulfate.

Experimental

The apparatus employed for this experiment was a flow system with nitrogen as the carrier gas.

The carrier gas was passed through the formic acid evaporator at a constant flow rate of 41 cc/min. The temperature of the evaporator was kept at 22±1°C and the room temperature was about 30—32°C. The carrier gas containing formic acid was allowed to flow through the reactor at the selected temperature. The concentration of formic acid in the carrier gas was determined by the concentration of carbon monoxide in the effluent gas when the formic acid was completely decomposed.

TABLE 1. DETAILS OF THE CATALYST USED

Sulfate	Molecular weight	Amounts doped on 10 g SiO_2 (g)
$ZnSO_4\cdot 7H_2O$	287.56	0.288
$NiSO_4\cdot 6H_2O$	262.87	0.263
$MnSO_4\cdot 4H_2O$	223.07	0.223
$MgSO_4\cdot 7H_2O$	246.50	0.246
$Fe_2(SO_4)_3\cdot 9H_2O$	562.04	0.281
$Cr_2(SO_4)_3\cdot 5H_2O$	482.30	0.241
$Al_2(SO_4)_3\cdot 16—18H_2O$	630.5—666.5	0.333
$CuSO_4\cdot 5H_2O$	249.7	0.250

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[1] K. Tanaka and A. Ozaki, This Bulletin, **40**, 1723 (1967); *J. Catalysis*, **8**, 1 (1967).

The catalyst was prepared as follows: a reagent-grade sulfate of about a 10^{-3} g-cation was supported on 10 g of silica gel (30—50 mesh Wako-gel-G was used) and dried at 100°C. Each experiment was carried out with 3.5 g of a catalyst. The details of the catalysts used are given in Table 1.

The reaction over these catalysts was completely the dehydration; therefore, the reaction was followed by the analysis of the carbon monoxide in the effluent gas by means of gas chromatography.

Results and Discussion

The reaction rate was calculated from the ratio of carbon monoxide to nitrogen in the effluent gas and from the flow rate of the carrier gas, nitrogen.

Figure 1 shows the rate of reaction at various temperatures. From this figure, the relative catalytic activities of the sulfates are in the following sequence:

$$Fe^{3+} > Cr^{3+} > Al^{3+} > Cu^{2+} \simeq Ni^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+}.$$

This sequence is very similar to that observed in the hydration of propylene.[2]

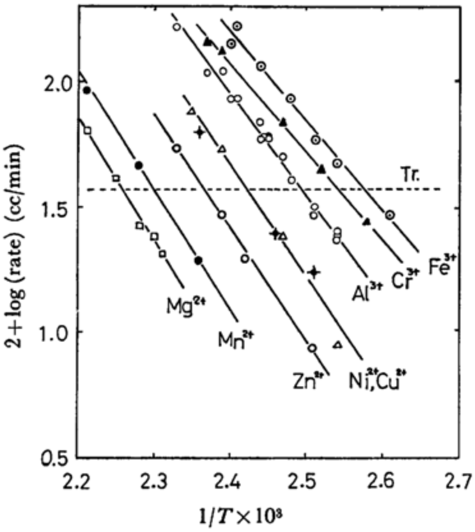

Fig. 1. Reaction rates at various temperatures.

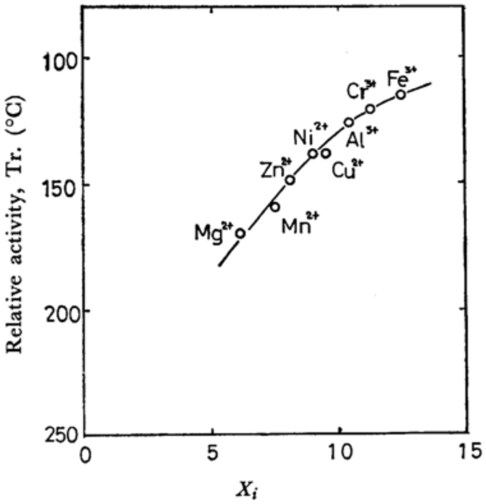

Fig. 2. Relative catalytic activity of sulfates. X_i denotes the electronegativity of metal ion.

The catalytic activity of each sulfate, characterized by the temperature at which the concentration of carbon monoxide in the carrier gas reached 1% (approximately an 11% conversion to the formic acid introduced), is plotted against the acidity parameter of the metal ion (X_i) in Fig. 2.

From this figure, it is obvious that the sulfate containing an acidic metal ion has a high catalytic activity and that the activity sequence is determined by the parameter, X_i.

On the other hand, it has been recognized that the surface acidity of sulfate is strongly affected by the temperature at which the sulfate is dehydrated. Tanabe *et al.*[3] ascribed this phenomena to a specific structure of the sulfate which appeared in the dehydration of sulfate.

In our experiment, however, the surface of the sulfates during the dehydration of formic acid was hydrated with the water produced, so the specific structure such as appearing in the rather rigorous dehydration of sulfate seemingly disappeared from the surface during the reaction. Accordingly, it may be concluded that the dehydration of formic acid is promoted by the acidity of the hydrated cation on the sulfate surface.

The parameter, X_i, is thus seemingly valuable for predicting the acidity and the catalytic activity of the hydrated surfaces.

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[2] Y. Ogino, *J. Catalysis*, **8**, 64 (1967).

[3] T. Takeshita, R. Ohnishi, T. Matui and K. Tanabe, *J. Phys. Chem.*, **69**, 4077 (1965).