Acid-base Concept and Catalytic Activity of Oxides

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In heterogeneous catalysis by metal oxide, many close correlations between the catalytic activity, including its selectivity, and the acidity of the oxide have been indicated. Most commonly the correlations have been discussed in connection with such typical acidic solid catalysts as silica-alumina. However, a more general treatment has been undertaken in this report to study the general trend of the catalytic activity of metal oxides.

Generally speaking, the strength of an acid is determined by the equilibrium constant between the acid and a base, such as water, for instance, in the following manner:

$$HA+H_2O=H_3O^+ +A^-$$

The more the equilibrium shifts to the right, the stronger the acid HA. It simultaneously depends upon the strength of the conjugate base, A^-; the weaker the conjugate base, thus with less of a tendency to combine with the proton, the stronger, the acid HA. Consequently, the strength of the acid depends upon the relative strength of the acid and its conjugate base.[1]

As is generally accepted, strong acids, such as sulfuric and nitride acids, are neuteralized with water molecules in an aqueous solution to show a "leveling effect," and their acidity practically drops to that of H_3O^+. Consequently, the stronger acids can stay comparatively strong in a medium, the protonated forms of which are stronger acids than the original acids.

Accordingly, it is considered that the proton on an oxide surface can behave as a strong acid if the oxide surface is more acidic, or less basic. The less basic the oxide surface is, and thus with less of a tendency to hold protons, the stronger the "protonated" surface of the oxide behaves as an acid, as the conjugate base is weak. When an acid comes into contact with an oxide surface, it can stay acidic if the protonated surface of the oxide is more acidic, while it is neutralized to form a salt if the oxide is more basic, showing a "leveling effect."

In the case of oxy-acids, it has been shown that the strength of the acid is closely correlated with the partial charge on the oxygen in the acid, or in the conjugate base, as shown in Fig. 1.[2] A high degree of deficiency of electrons on the oxygen is associated with a high acidity of the acid. For instance, as a more electronegative atom is added to an oxy-acid, the electronegativity of the acid increases, with a low partial charge on the oxygen, and the strength of the acid increases. The electronegative atom attracts electrons to itself until the electronegativity of each atom in the acid molecule is equalized. The acidities of hypochlorous, chlorous, chloric and perchloric acids are examples.

The acidity of the oxide surface can be treated in a similar manner, and the partial charge on the oxygen in the oxide can be correlated with the acidity of the oxide surface. The data on the partial charge on the

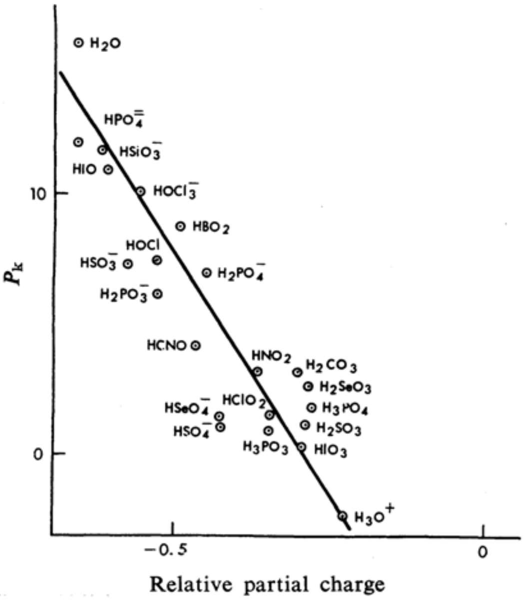

Fig. 1. The dependence of acidity upon relative partial charge on oxygen in oxy-acids. (by Sanderson[2])

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1) E.g. C. A. Vander Werf, "Acids, Bases, and the Chemistry of the Covalent Bond," Reinhold Pub. Corp., N. Y. (1961).

2) R. T. Sanderson, "Chemical Periodicity," Reinhold Pub, Corp., N. Y. (1960).

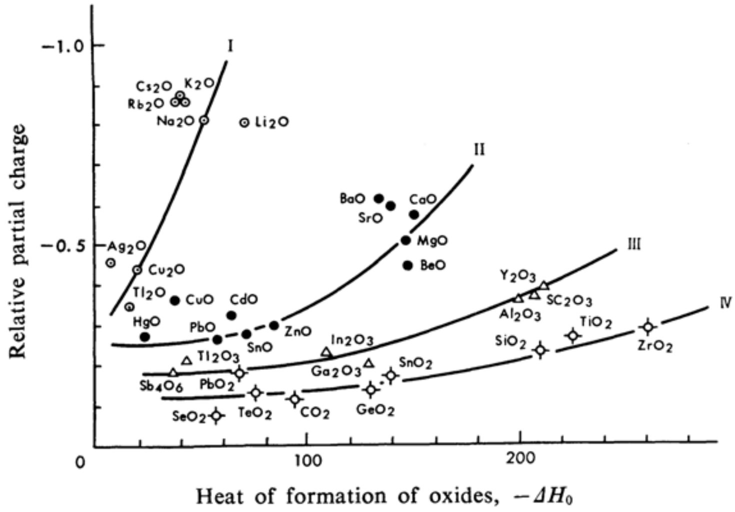

Fig. 2. The relation between the partial charge on oxygen and the heat of formation of oxides (kcal./metal atom).

oxygen in the oxides, which are given by Sanderson,[2] are not available in many oxides. However, as far as all the available data are concerned, a reasonably good correlation can be established between the partial charge and the heat of the formation of the oxides, as is shown in Fig. 2. In the figure, it may be seen that the partial negative charge on oxygen in the oxide becomes lower as the oxidation number of metals increases, and also as the heat of formation of the oxides decreases.

The metals which have lower heats of formation of the oxides have a comparatively higher electronegativities, and the difference between their electronegativities and that of oxygen is small, and they have a more covalent nature in the bond, which results in a low partial charge of oxygen and a high acidity. In these ways, the acid-base concept is applicable to the surface catalysis, especially those by oxide catalysts.

An example where the acidity of the oxide surface seemingly plays a role in the catalysis is the decomposition of alcohol and formic acid.[3-8] In the decomposition of alcohol and formic acid, a common trend has been observed in their selectivity, as is shown in Fig. 3,[3] and the dehydration reaction is promoted by the acid, while the dehydrogenation reaction is promoted by the base, phenomena which are analogous to the homogeneous catalytic decomposition of alcohol and formic acid. If we plot the data by Mars[3] against the heat of formation, $(-\Delta H_0)$, Fig. 4 is obtained. Though the number of the oxide in the figure is not large enough, it may be concluded that the selectivity to dehydrogenation increases as the valency of the metal decreases (that is, as the oxide becomes more basic).

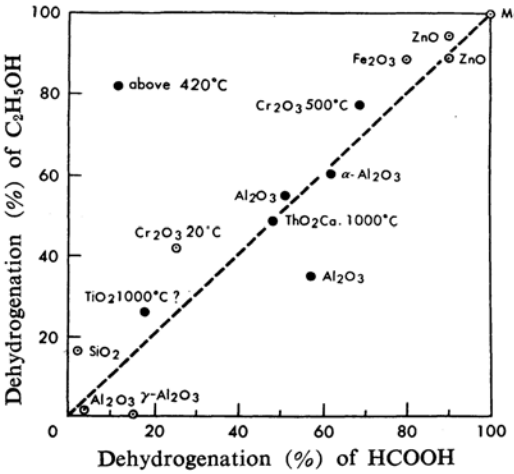

Fig. 3. The selectivity in the decomposition of formic acid and ethyl alcohol on metal oxides. (by Mars[3])

As to the effect of the heat treatment of the catalyst on the selectivity, Schwab[4] has revealed that it reduces the dehydration rate, while, in many cases, it increases the dehydrogenation rate. When the catalyst is treated

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[3] P. Mars, "The Mechanism of Heterogeneous Catalysis," Ed. by J. H. de Boer, Elsevier Pub. Co., Amsterdam (1960), p. 49.

[4] G. M. Schwab and E. Schwab-Agallides, *J. Am. Chem. Soc.*, **71**, 1806 (1949).

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[6] J. H. de Boer and J. M. Vleeskens, *Koninkl. Ned. Akad. Wetenschap., Proc. Ser. B.*, **60**, 234 (1957); **61**, 2, 85 (1958).

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[8] J. J. F. Scholten, P. Mars, P. G. Menon and R. van Hardeveld, Third International Congress on Catalysis, Amsterdam, 1964.

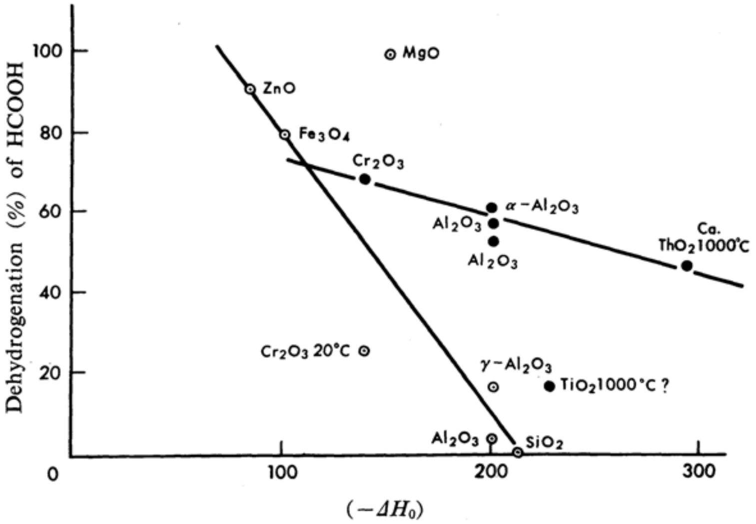

Fig. 4. The selectivity to dehydrogenation of formic acid on metal oxides and their heats of formation (kcal./metal atom).

at higher temperatures, with less oxygen on the surface, the surface behaves in a more basic manner, having a higher partial charge of oxygen, much like such general Brönsted oxy-acids as hypochlorous acid.

The general correlation of the catalytic activity with its acidity is also shown by the retardation of the dehydration reaction by basic substances: The addition of potassium hydroxide or calcium hydroxide reduces the catalytic activity of alumina and silica in the dehydration markedly.⁵⁾

The kinetics of the overall reaction can also be interpreted on the same basis. The dehydration of formic acid is zero-order in formic acid and is not slowed down by the reaction products, while the decomposition of alcohol is retarded by water and is between zero- and first-order in alcohol. The strength of the acidity is in the decreasing order; formic acid>water>alcohol, which is the same order as with the strength of the adsorption on oxide surface. Accordingly, the kinetic behavior of the overall reaction may also reasonably be explained on the common basis.

Eucken attempted to correlate the selectivity of the decomposition with the quantity:

$$\eta=\frac{(\text{cation radius})^3}{(\text{mol. volume per cation})\,(\text{charge of cation})}$$

while Mars³⁾ worked with;

$$\left(\frac{\text{cation radius}}{\text{anion radius}}\right)^3\frac{1}{(\text{cation charge})^2}$$

The dehydration proceeds when the cation radius is small, that of the anion is large, and the charge of the cation is high. From the electrostatic point of view, a smaller cation radius implies more of a tendency to attract electrons (a stronger acid), while the higher cation charge and the larger anion radius are associated with the acidic property of the oxide. Accordingly, $1/\eta$ is a parameter of the electronegativities or the acidity of metal oxides. Mars suggested the possibility that formic acid donates a proton to the catalyst to result in dehydrogenation, as in the case of a metal catalyst.³⁾ The basicity of the catalyst surface would be associated with the dehydrogenation selectivity in a similar way.

In the hydration of propylene, the catalytic activities of metal sulfates are as follows, in

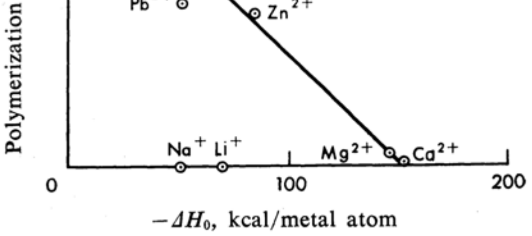

Fig. 5. The catalytic activity of metal phosphates for the polymerization of isobutylene and the heats of formation of the corresponding oxides.

decreasing order:⁹⁾ $Fe^{3+} > Al^{3+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+} > Ni^{2+} > Mn^{2+} > Mg^{2+} > K^{+}$, Na^{+}. They obey the general acidity rule—the more acidic ion has a higher activity, much as in the dehydration of alcohol. The sulfates which contain acidic, or less basic, metal ions, have much catalytic activity and, if the charge of metal ions is the same, the activity is high when $-\Delta H_0$ is low. The catalytic activity of phosphates for the polymerization of isobutylene¹⁰⁾ is shown in Fig. 5, where acidic salts are active in the reaction.

The interpretation of the selectivity of the oxide catalyst on the basis of the semi-conductor does not seem likely, for magnesium oxide and silicon dioxide are both insulators and also both the dehydrogenating zinc oxide and the dehydrating titanium(IV) oxide are seemingly *n*-type semi-conductors, as Mars pointed out previously.³⁾ Thus the acid-base concept of oxide seems to be really useful in interpreting their catalytic behavior.

The chemisorption of gases on the metal surface has been successfully correlated with the heat of the formation of the highest oxide of the metal, and this heat of formation and the electronegativities of gases approximately determine the initial heat of chemisorption of any gases on many metals, according to the available data.¹¹⁾ The catalytic activity of metals, accordingly, has also been correlated with the heat of the formation of the metal oxide,¹²⁾ and, in a similar manner, that for metal oxide has been treated in connection with the heat of the oxide, or with its acidity.

Summary

The catalytic activity of metal oxide has been correlated with the acidity of the oxide surface. The acidity depends upon the partial charge on the oxygen in the oxide and also upon the heat of the formation of the oxide. Consequently, the catalytic behavior may be correlated with the heat of the formation of the oxide, as in the cases of the chemisorption of gases and catalytic activity by metals.

The decomposition of formic acid and alcohol and the polymerization of isobutylene have been treated on the basis of this concept, and the selectivity, or activity, of these reactions, their reaction kinetics, and also the effect of heat treatment have been discussed.

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