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Acid-Base Properties and Catalytic Activity of Solid Surfaces

KEN-ICHI TANAKA AND ATSUMU OZAKI

From the Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo, Japan

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Acid-base properties of the solid surfaces, oxides, sulfates, and acid phosphates, and their catalytic behavior for the hydration of propylene, the polymerization of isobutylene and the polymerization of acetaldehyde are discussed in terms of a generalized electronegativity of the metal ion (X_i). It is found that the acidity and the catalytic activity increase with the parameter X_i. Such general trends are explained by the inductive effect of the metal ions in the catalysts.

INTRODUCTION

A number of definitions of the acid-base concept have been proposed to describe the acidity and the basicity of molecules or ions. According to Lewis's definition, acidity and basicity are electron-accepting and electron-donating properties which contribute to formation of a covalent bond. Accordingly, as a first approximation, the acidity could be expressed by the electronegativity scale; the larger the electronegativity, the stronger the electron-accepting power.

In this paper, it is shown that the acid-base properties of the solid surfaces and their catalytic behavior are strongly affected by the inductive effect of the metal ions in the solids.

ACIDITY OF METAL IONS

As acidity is characterized as a tendency to attract electrons to form a covalent bond, the acidity of a metal ion according to the Lewis concept may increase with its electron-withdrawing power or electronegativity.

According to Iczcowski and Margrawe (*2*), the electronegativity of the metal ion (X_i) is related to its charge (Z) and the ionization potential (I) in the following way:

$$X_i = (\partial I/\partial Z) \qquad (1)$$

The successive ionization potential (I) of an atom is generally given by the following equation:

$$I = aZ + bZ^2 + cZ^3 + \cdots \qquad (2)$$

It is well known that the ionization potential of a nonmetallic element is approximately expressed by a quadratic equation. If it is permissible to extend this approximation to metallic elements, the electronegativity of the metal ion would be expected to change linearly with its charge, as Sanderson (*3*) has pointed out

$$X_i = a + 2bZ = (1 + 2bZ/X_0)X_0 \qquad (3)$$

where X_0 is the electronegativity of the neutral atom ($Z = 0$) given by Pauling. By taking the value of $b/X_0(=b/a)$ in Eq. (3) as unity,* a generalized electronegativity of

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* The values of b/a calculated from the following equations are approximately unity:

$$I_1 = a + b, \qquad I_1 + I_2 = 2a + 4b$$

$$a/b = (3I_1 - I_2)/(I_2 - I_1)$$

(contd.)

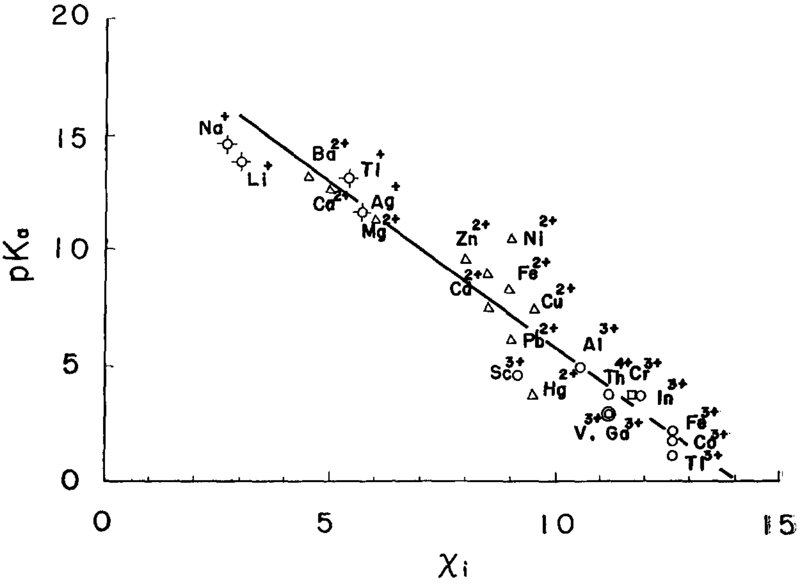

FIG. 1. Acid ionization constants for aqueous metal ions at 25°C.

the metal ion is found to be as follows (*1*):

$$X_i = (1 + 2Z)X_0 \quad (4)$$

The most familiar process associated with metal ion acidity is the ionization (hydrolysis) of the "aqua-ion" in solution. The ionization of the aqua-ion in water is frequently represented by an equation such as

$$M(H_2O)_m^{a+} + H_2O \rightleftharpoons [M(H_2O)_{m-1}(OH)]^{(a-1)+} + H_3O^+ \quad (5)$$

which implies that an aqueous solution of a metal ion gives an acidic solution when the equilibrium shifts to the right.

Both Pauling's neutrality principle (*4*) and Sanderson's electronegativity equalization principle (*3*) suggest that the acidity of an aqua-ion increases with the electronegativity of the central metal ion. Figure 1 is a plot of the pK values of Eq. (5) against the parameter X_i obtained by Eq. (4). The correlation observed in this figure demonstrates the expected effect of the central ion's electronegativity, and thus the generalized electronegativity X_i may be regarded as a semiempirical acidity parameter of the metal ion.

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where I_1 and I_2 are the first and second ionization potentials, respectively.

Be											
1.0											
Mg											Al
1.0											−0.06
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
1.0	*1.1*	*1.0*	*0.7*	0.4	*0.8*	*0.8*	*0.7*	0.5	0.2	*1.2*	−0.08
Sr	Y	Zr	Nb	Mo			Rh	Pd	Ag	Cd	In
1.2	*1.3*	*1.0*	—	—			—	0.4	0.1	*1.3*	−0.21
Ba											
1.2											
	La	Ce	Sm	Eu							
	0.9	*0.8*	*0.9*	*1.0*							

Italics indicate $b/a = \sim 1.3\text{–}0.7$

ACID-BASE PROPERTIES OF A SOLID SURFACE

It is generally recognized that both the structure and the character of the surface layer are different from those of the lattice and are affected by the hydration or the adsorption of gases or ions. It would be expected that the ionic character of the surface layer might be increased by surface hydration as is usually observed in the hydration of salt molecules.

When an insoluble oxide is suspended in water, the surface is hydrated. The hydroxyl groups or the water molecules coordinated to the metal ion of the hydrated surface may ionize as an acid or as a base depending on the proton activity of the surrounding liquid phase.

In the case of oxides, the potential-determining ions of which are H^+ and OH^-, the ionization of the surface is accordingly expressed as follows:

$$C^0 + A^+ \rightleftharpoons C^+ \qquad K_b$$
$$C^0 \rightleftharpoons C^- + A^+ \qquad K_a$$

where C^+, C^0, and C^- are, respectively, positive, zero, and negative charge densities of the surface, A^+ is the activity of the proton in equilibrium solution and K_a, K_b are the equilibrium constants.

The tendency of such surface ionization to occur can be estimated from the isoelectric point or zero point of charge of the surface. Zero point of charge (zpc), that is, the pH of the equilibrium solution at which the surface is uncharged, can be related to the equilibrium constants K_a and K_b as follows:

$$K_a = (C^-)(A^+)/(C^0)$$
$$K_b = (C^+)/(C^0)(A^+)$$

at zero point of charge, $C^+/C^- = 1$, the activity of the hydrogen ion corresponding to the zpc is given by the equation

$$(a_0{}^+)^2 = K_a/K_b$$
$$(\text{zpc}) = \tfrac{1}{2}(pK_a - pK_b)$$

This equation demonstrates that the acidic nature of the hydrated surface is characterized by its zero point of charge. Figure 2 is a plot of zpc's which are summarized in a recent review by Parks (*5*) against the parameter X_i of the corresponding metal ion. The linear relation in this figure implies that the standard free energy change asso-

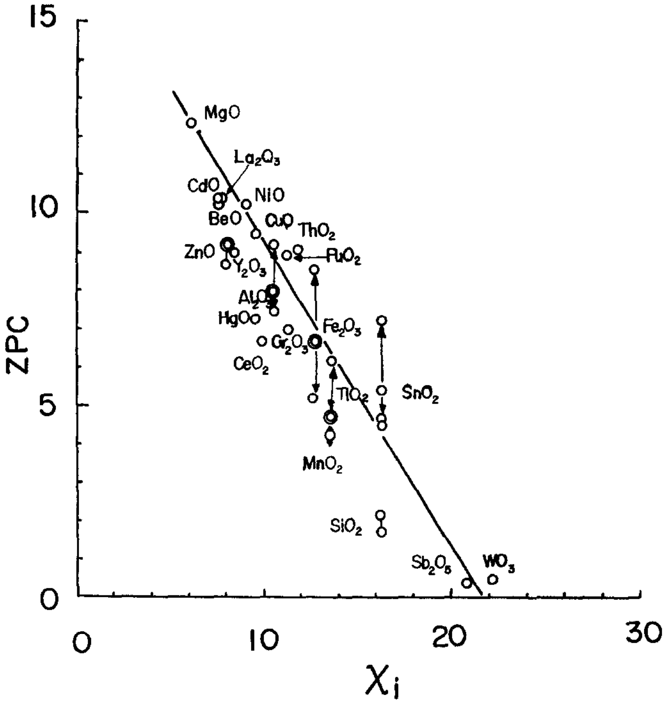

FIG. 2. The relationship between the zero point of charge of oxides and X_i.

ciated with the above equilibrium will change linearly with the parameter X_i and that the acidity of the hydrated surfaces depends on the extent to which they are polarized by the metal ions.

Healy and Fuerstenau (*6*) pointed out a linear relationship between the heat of immersion and zpc for a few oxides. Figure 3 gives a plot of the heat of hydration of oxides, $1/m(\mathrm{MO}_m) + \mathrm{H_2O} \rightarrow 1/m[\mathrm{M(OH)}_{2m}]$, as a function of X_i. It is obvious from Fig. 2 and Fig. 3 that the heat of hydration of the oxides increases with its zpc. This trend suggests that the heat of immersion of the oxide will generally increase with the heat of hydration of the oxide.

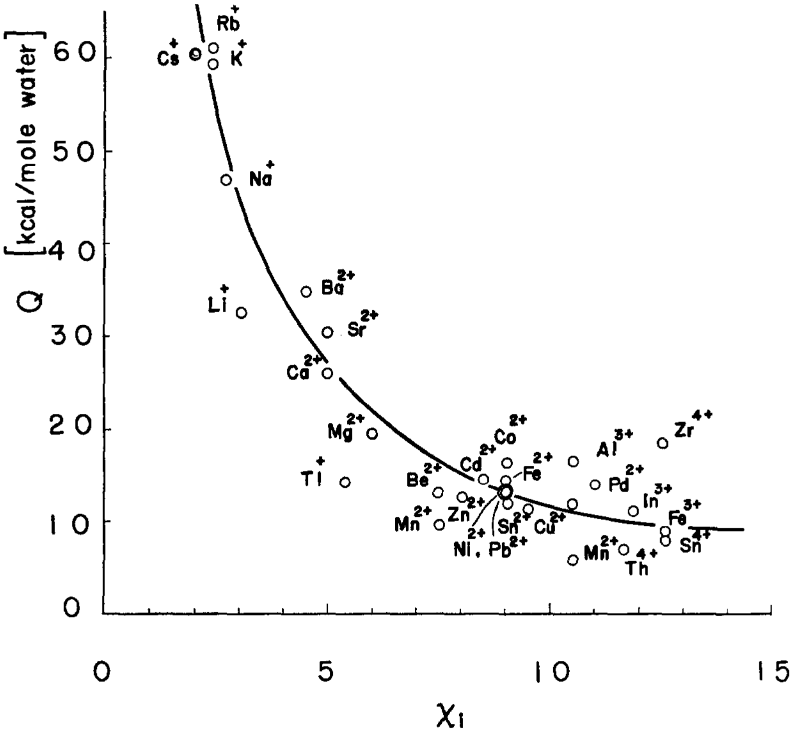

FIG. 3. The relationship between the heat of hydration of oxides per mole of water and X_i.

ACID-BASE PROPERTIES AND CATALYSIS

If it is permissible to apply the parameter X_i to other solid surfaces, a general tendency in the catalytic behavior of solid surfaces for reactions which are mainly promoted by the acidic nature of the surfaces is expected to be found.

Sulfates

It is well known that the hydration reaction of propylene is catalyzed by acid. Ogino (*7*) has studied the hydration of propylene over sulfates, and found the following activity sequence of the sulfates: $\mathrm{Fe^{3+}} > \mathrm{Al^{3+}} > \mathrm{Cr^{3+}} > \mathrm{Cu^{2+}} > \mathrm{Zn^{2+}} > \mathrm{Co^{2+}} > \mathrm{Cd^{2+}} > \mathrm{Ni^{2+}} > \mathrm{Mn^{2+}} > \mathrm{Mg^{2+}} > \mathrm{K^+}, \mathrm{Na^+}$. If we plot the activity of the sulfates against the parameter X_i, Fig. 4 is obtained, where the catalytic activity is characterized by the temperature at which the conversion to alcohol reaches 1% under a constant flow rate.

Takita and Noro (*8*) found that the polymerization of acetaldehyde is promoted by sulfates and the catalytic activity of the sulfates is strongly affected by the pretreatment temperature of the catalysts.

If we plot the catalytic activity of the sulfates which are dehydrated at a rather low temperature (below 100°C) against the acidity parameter X_i, Fig. 5 is obtained. It is obvious from this figure that the catalytic

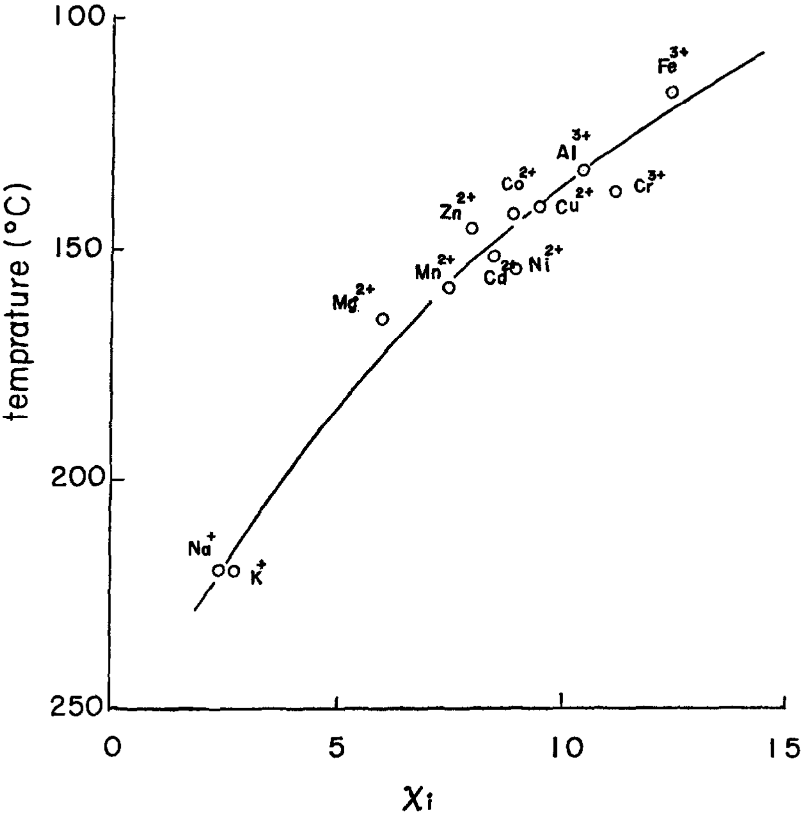

Fig. 4. The catalytic activity of sulfates for the hydration of propylene as a function of X_i, where the catalytic activity is characterized by the temperature at which the conversion reaches the fixed value 1% at a given flow rate.

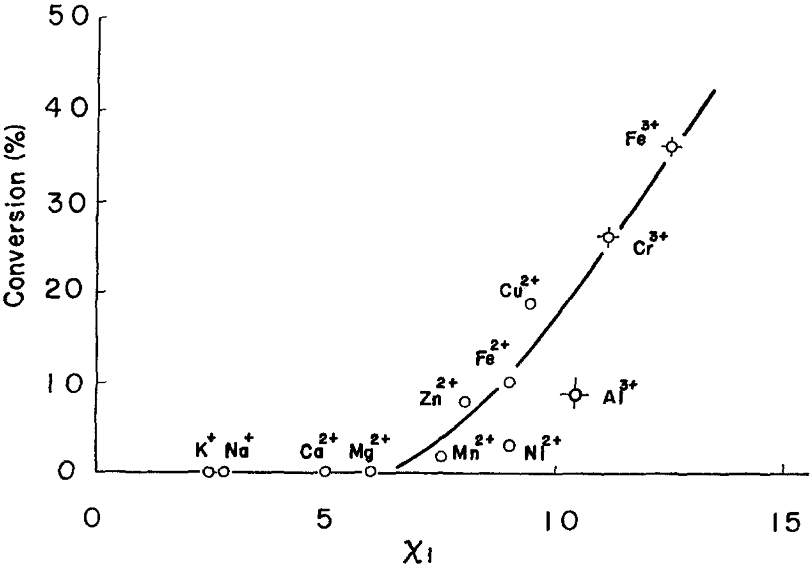

Fig. 5. The catalytic activity of sulfates for acetaldehyde polymerization as a function of X_i.

activity of the partly hydrated sulfates increases steadily with the parameter X_i. However, the activity of the sulfates dehydrated at higher temperatures shows no reasonable correlation with the parameter X_i. Such a marked influence of the treatment temperature on the catalytic activity may be caused by a specific structure of the catalysts produced by the dehydration, and its catalytic action may be far more complicated.

Acid Phosphates

It is well known that the surfaces of solid acids are usually not homogeneous but are heterogeneous in acid strength. The origin of such heterogeneity has so far not been established, making it difficult to elucidate the interrelation between the surface acidity and its catalytic action. An acid salt or an ion-exchange resin would be expected to be homogeneous in acid strength, accordingly it is convenient to discuss the catalytic action of the surface acidity.

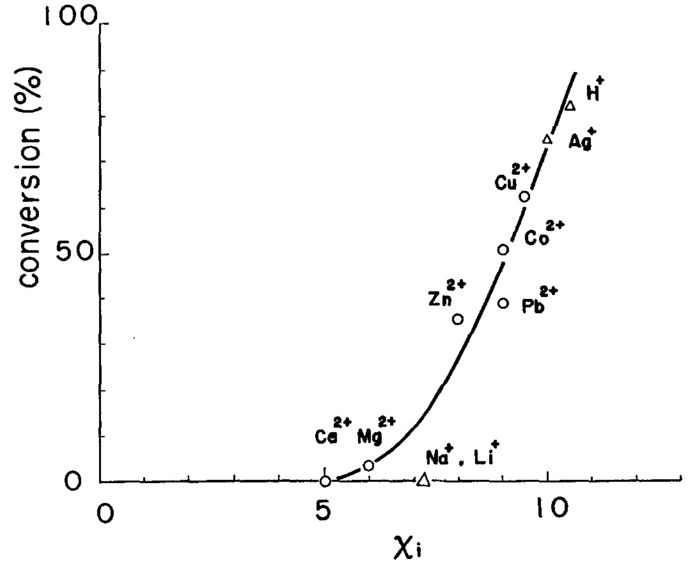

FIG. 6. The catalytic activity of acid phosphates for isobutylene polymerization as a function of X_i.

Shima and Ohta (*9*) found that some acid phosphates promote the polymerization of isobutylene, but their normal salts, having no proton in the molecule, exhibit no catalytic activity for this reaction. From these facts they concluded that the reaction proceeds via the proton mechanism.

If we plot their data against the parameter X_i, Fig. 6 is obtained, where X_i values for monovalent ions (Li^+, Na^+, Ag^+, and H^+) are tentatively taken as the values for $(LiH)^{2+}$, $(NaH)^{2+}$, $(AgH)^{2+}$, and $(HH)^{2+}$ calculated by the geometric mean of the components* in order to compare the catalytic activity of acid phosphates of a monovalent ion (H_2MPO_4) with those of a divalent one ($HMPO_4$). It is concluded that the catalytic activity of the acid phosphates increases with the parameter X_i of the metal ion. This fact demonstrates that the ion of larger X_i value attracts electrons more strongly to reduce the partial negative charge of the oxygen atom in the acid phosphate or in its conjugate base of the surface layer and to increase the Brönsted acidity and its catalytic activity.

The parameter X_i allows rough prediction of the surface acidity and seems to be useful in interpreting the general behavior of heterogeneous catalysis.

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* The acid ionizations to be related here are

$$HMPO_4 \leftrightarrows H^+ + MPO_4^-$$
$$H_2MPO_4 \leftrightarrows H^+ + HMPO_4^-$$

Accordingly, the effect of electronegativity of M^{2+} or $(HM)^{2+}$ on the ionization is to be referred to.

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