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The φ-Classification of Metal Oxides for Heterogeneous Oxidation Catalysts

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The plot of $(-\Delta H_o^{-1})$ against (X_i^{-1}) reveals that: (i) metal oxides may be divided into two kinds depending on the oxidizing ability by a border line expressed as $\phi_o(-\Delta H_o^{-1}, X_i^{-1}) = 0$, and (ii) they may be classified into six groups, where $-\Delta H_o$ is the heat of formation of metal oxide and where X_i is the electronegativity of the metal ion. This classification is in accordance with that derived from the catalytic activity for acid- and/or base-catalyzed reactions. The relations of $(\Sigma I_i/r)$ with (X_i^{-1}) and of Z/r with X_i were studied, where ΣI_i is the sum of the ionization potentials, r is the radius of the metal ion, and Z is the valence of the metal ion. The metal oxides can also be divided into two kinds by a straight line, $\phi_o(\Sigma I_i/r, X_i^{-1}) = 0$ or $\phi_o(Z/r, X_i) = 0$, and classified into six groups. On the other hand, metal oxides may be classified depending on their softness or hardness by means of a border line expressed as $\varphi_o[(-\Delta H_o^{-1})', (X_i^{-1})'] = 0$, where $(-\Delta H_o^{-1})'$ and $(X_i^{-1})'$ are obtained by turning the coordinates of $(-\Delta H_o^{-1})$ and (X_i^{-1}) counterclockwise for 36°. The classification based on the softness or hardness of an acid can also be made by a straight line expressed as $\varphi_o(\Sigma I_i/r, X_i^{-1}) = 0$ or $\varphi_o(Z/r, X_i) = 0$. The softness or hardness of various metal ionic acids was calculated from $\varphi[(-\Delta H_o^{-1})', (X_i^{-1})']$, and $\varphi(Z/r, X_i)$, and then compared with those values previously reported.

INTRODUCTION

It has been proposed (1) that the main requirements for an oxidation catalyst are: $F(1)$: the activation of the reactant molecule; $F(2)$: the ability to regenerate active oxygen sites, and $F(3)$: the reactivity of the oxygen sites.

$F(1)$ is attributed to the acid–base-type interaction between catalyst and reactant. $F(2)$ is the ability to perform the reaction step:

$$M^{(n-x)+} + (x/4)\,O_2 \rightarrow M^{n+} + (x/2)\,O^{2-}. \quad (1)$$

According to an assumption that the electron-donating ability of a metal ion in a lower oxidation state is associated with the electron-donating ability of O^{2-} of metal oxides in a higher oxidation state, $F(2)$ is estimated from the basic properties (number and strength) of metal oxides in a higher oxidation state. Thus, it is written as

$$F(2) = (\text{basicity}) \cdot f(\text{base strength}). \quad (2)$$

$F(3)$ is the ability to perform the reaction step shown in Eq. (3); it is dependent on both the metal–oxygen bonding strength (M–O) and the number of active oxygen sites (basicity):

$$M^{n+}\text{–}O^{2-} + R \rightarrow M^{(n-x)+} + RO. \quad (3)$$

Thus, $F(3)$ is written as

$$F(3) = (\text{basicity}) \cdot f(\text{M–O bond strength}). \quad (4)$$

It should be borne in mind that in addition to the function of catalyst, $F(3)$, the reaction step shown in Eq. (3) is also dependent on the reactivity of reactant, e.g., the reducing power and/or the extent of activation of reactant.

The "redox cycle" consists of the two steps shown in Eqs. (1) and (3). Therefore, at least two functions, $F(2)$ and $F(3)$, are required to perform the "redox cycle." As regards these two functions, it is thought that they are not exactly dependent on each other; that is, they do not completely com-

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pensate for each other, because they are different in nature, to some extent. This may be the main reason why we cannot succeed in fully regulating the catalytic action with only one characteristic of metal oxide, such as its metal–oxygen bonding strength or its acid-base property.

The object of the present paper is to explore the presence of regularities, though the study is on a semiempirical and semiquantitative level at this stage, by introducing unique parameters, i.e., the ϕ-function, which consists of two characteristics, one reflecting the metal–oxygen bonding strength and the other reflecting the electron-donating ability.

RESULTS

The Classification of Metal Oxides from the $\phi(-\Delta H_o^{-1}, X_i^{-1})$ Function

First, the heat of formation of metal oxide per gram atom of oxygen ($-\Delta H_o$) and the electronegativity of the metal ion corresponding to the metal oxides (X_i) (2) were chosen as scales of $F(3)$ and $F(2)$, respectively. The values for various single oxides are plotted in Fig. 1. The metal oxides can be divided into two kinds, oxides having an oxidizing function and those having no oxidizing function, by means of a parabola equation. However, the parabola equation is very complex; therefore, this system is too inconvenient for further application.

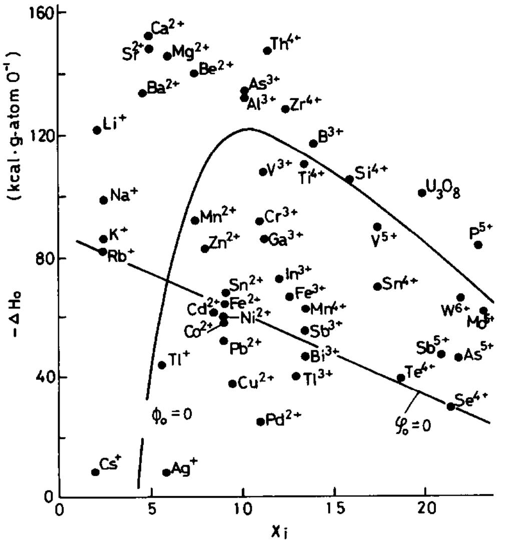

FIG. 1. Relation between $-\Delta H_o$ and X_i.

To illustrate the diagram more simply, the coordinates of the parabola equation must be transformed. With this in mind, ($-\Delta H_o^{-1}$) and (X_i^{-1}) were chosen as scales of $F(3)$ and $F(2)$, respectively. The relation between ($-\Delta H_o^{-1}$) and (X_i^{-1}) is shown in Fig. 2. The metal oxides are divided by a border line expressed as

$$\phi_o(-\Delta H_o^{-1}, X_i^{-1}) = -\Delta H_o^{-1} - 1.95(0.1 - X_i^{-1})^2 - 0.0077 = 0, \quad (5)$$

$\phi_o > 0$: oxides having an oxidizing function,

$\phi_o < 0$: oxides having no oxidizing function.

The metal oxides belonging to the $\phi_o > 0$ group are aligned with one of four straight lines, suggesting that this kind of oxide can be classified into four groups. The straight lines are expressed by the following equations:

Group A: Mo^{6+}, W^{6+}, V^{5+},

$$\phi_A(-\Delta H_o^{-1}, X_i^{-1}) = -\Delta H_o^{-1} + 0.36\, X_i^{-1} - 0.033 = 0. \quad (6)$$

Group B: Te^{4+}, As^{5+}, Sb^{5+}, Sn^{4+}, Ti^{4+},

$$\phi_B(-\Delta H_o^{-1}, X_i^{-1}) = -\Delta H_o^{-1} + 0.58\, X_i^{-1} - 0.051 = 0. \quad (7)$$

Group B′: Tl^{3+}, Bi^{3+}, Sb^{3+}, Co^{3+}, Fe^{3+}, Mn^{4+}, In^{3+}, Ga^{3+}, Cr^{3+}, V^{3+}, As^{3+},

$$\phi_{B'}(-\Delta H_o^{-1}, X_i^{-1}) = -\Delta H_o^{-1} + 1.29\, X_i^{-1} - 0.12 = 0. \quad (8)$$

Group C: Pd^{2+}, Hg^{2+}, Cu^{2+}, Sc^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Fe^{2+}, Sn^{2+}, (Zn^{2+}, Mn^{2+}),

$$\phi_C(-\Delta H_o^{-1}, X_i^{-1}) = -\Delta H_o^{-1} + 2.33\, X_i^{-1} - 0.24 = 0. \quad (9)$$

On the other hand, the oxides of the $\phi_o < 0$ group can be classified into three groups

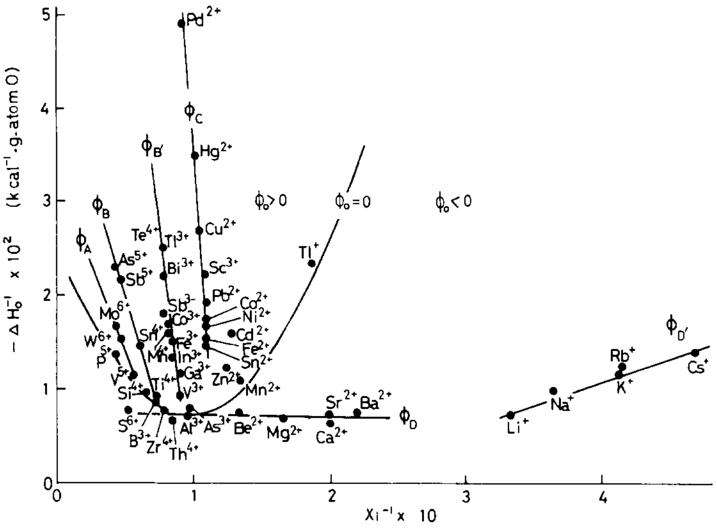

FIG. 2. Relation between $(-\Delta H_o^{-1})$ and (X_i^{-1}).

by means of the following three equations:

Group A′: P^{5+}, Si^{4+}, B^{3+}, Zr^{4+}, As^{3+}, Al^{3+},

$$\phi_o(-\Delta H_o^{-1}, X_i^{-1}) = 0. \quad (5)$$

Group D: oxides of alkaline earth metals,

$$\phi_D(-\Delta H_o^{-1}, X_i^{-1}) = -\Delta H_o^{-1} + 0.0037\,X_i^{-1} - 7.9 \times 10^{-3} = 0. \quad (10)$$

Group D′: oxides of alkali metals,

$$\phi_{D'}(-\Delta H_o^{-1}, X_i^{-1}) = -\Delta H_o^{-1} - 0.051\,X_i^{-1} + 9.3 \times 10^{-3} = 0. \quad (11)$$

It should be noted that this classification of metal oxides is in accordance with that obtained from the catalytic activities for acid- and/or base-catalyzed reactions (*1*).

The Classification of Metal Oxides on the Basis of the $\phi(\Sigma I_i/r, X_i^{-1})$ *Function*

Next, the value of $\Sigma I_i/r$, where ΣI_i is the sum of the ionization potentials of the metal ion with a valence of i and where r is the radius of the metal ion, is chosen as scale of F(3). The relation between $\Sigma I_i/r$ and X_i^{-1} is shown in Fig. 3.

The border line between the oxidation catalysts and the nonoxidation catalysts is expressed by the following linear equation:

$$\phi_o(\Sigma I_i/r, X_i^{-1}) = \log(\Sigma I_i/r) + 12.6\,X_i^{-1} - 3.1 = 0, \quad (12)$$

$\phi_o(\Sigma I_i/r, X_i^{-1}) < 0$: oxides having an oxidizing function,

$\phi_o(\Sigma I_i/r, X_i^{-1}) > 0$: oxides having no oxidizing function.

The metal oxides can be classified in the same way as in the case of the above-mentioned $\phi(-\Delta H_o^{-1}, X_i^{-1})$ function. The four border lines are expressed as follows:

$$\phi_1(\Sigma I_i/r, X_i^{-1}) = \log(\Sigma I_i/r) - 57.1\,X_i^{-1} + 0.71 = 0, \quad (13)$$

$$\phi_2(\Sigma I_i/r, X_i^{-1}) = \log(\Sigma I_i/r) - 53.8\,X_i^{-1} + 2.0 = 0, \quad (14)$$

$$\phi_3(\Sigma I_i/r, X_i^{-1}) = \log(\Sigma I_i/r) - 37.2\,X_i^{-1} + 2.2 = 0, \quad (15)$$

$$\phi_4(\Sigma I_i/r, X_i^{-1}) = \log(\Sigma I_i/r) - 27.6\,X_i^{-1} + 2.4 = 0. \quad (16)$$

In the case of oxides having an oxidizing function ($\phi_o < 0$),

Group A oxides: $0 < \phi_1$,

Group B oxides: $\phi_1 < 0 < \phi_2$,

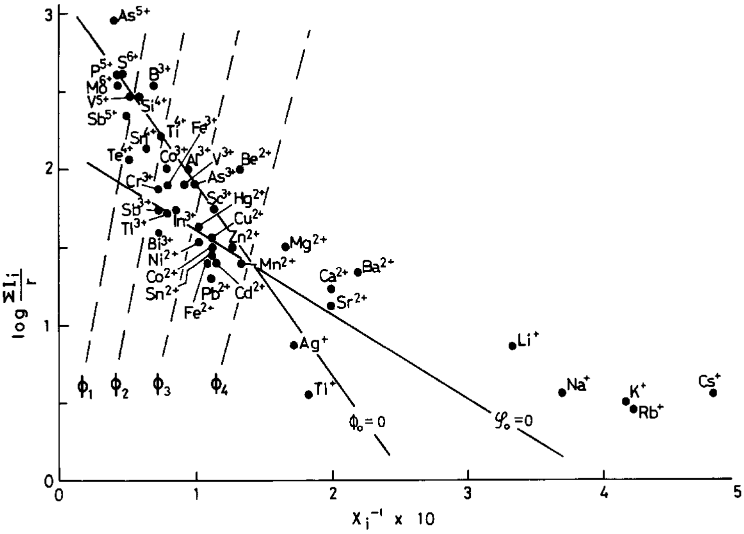

FIG. 3. Relation between log $(\Sigma I_i/r)$ and (X_i^{-1}).

Group B′ oxides: $\phi_2 < 0 < \phi_3$,

Group C oxides: $\phi_3 < 0 < \phi_4$,

Oxides of Ag^+ and Tl^+: $\phi_4 < 0$.

In the case of oxides having no oxidizing function ($\phi_o > 0$),

Group A′ oxides: $0 < \phi_3$,

Group D and D′ oxides: $\phi_4 < 0$.

The border lines obtained in the present study were compared with the results which had previously been reported, such as the catalytic activity for the dehydration of 2-propanol (r_p) (*1*), the negative charge of oxygen in oxides of the first and second periodic elements and of full *d*-electron elements ($-\delta_o$) (*3*), and the maximum acid strength of oxides ($H_{o_{max}}$ (*4*). The results are shown in Table 1.

The Classification of Metal Oxides from the Softness and Hardness of Acids

Peason (*5*) derived the concept of the softness and hardness of acids and bases from polarizability and quantitatively associated the concept with various physicochemical properties, such as the ionization potential and the oxidation–reduction potential. At present, the concept is widely applied in the field of chemistry.

However, it should be borne in mind that the action between an acid and a base consists of the following three aspects: (i) electrostatic action, including ionic polariza-

TABLE 1

Relation of $\phi(\Sigma I_i/r, X_i^{-1})$ Border Lines with r_p, $-\delta_o$, and $H_{o_{max}}$

Range	$0 < \phi_1$	$\phi_1 < \phi_2, \phi_3$	$\phi_3 < 0 < \phi_4$	$\phi_4 < 0$
r_p[a]	$\sim 5 \times 10^{-5}$–5×10^{-4}	$\sim 5 \times 10^{-6}$–5×10^{-5}	$< 5 \times 10^{-6}$	$< 5 \times 10^{-6}$
$-\delta_o$[b]	<0.18	~0.18–0.25	~0.25–0.37	~0.37–0.6
$H_{o_{max}}$[c]	~0–5	~0–5	~5–8	>8

[a] Ref. (*1*).
[b] Ref. (*3*).
[c] Ref. (*4*).

tion; (ii) the formation of a covalent bond with electron donor and acceptor, and (iii) the back-donation of π-electrons from acid to base. In this respect, Peason paid attention merely to (i) the electrostatic aspect. Therefore, his approach may, in a sense, be imperfect.

In this study, we adopted $-\Delta H_o$ and Z/r as scales of (i) the electrostatic function, and X_i as a scale of the ability to form a covalent bond [functions (ii) and (iii)], in order to study the softness or hardness of acids, taking into account two chemical parameters, where Z is the valence of the metal ion and Z/r is defined as the ionic potential (*6*).

To illustrate the diagram more simply, new parameters, $(-\Delta H_o^{-1})'$ and $(X_i^{-1})'$, were introduced; they were obtained by turning the coordinates of $(-\Delta H_o^{-1})$ and (X_i^{-1}) (shown in Fig. 2) counterclockwise for 36°. The relation between $(-\Delta H_o^{-1})'$ and $(X_i^{-1})'$ is shown in Fig. 4.

Metal oxides can be divided by a border line into two kinds, soft acids and hard acids (*5, 7, 8*). The border line is expressed as

$$\varphi_o[(-\Delta H_o^{-1})', (X_i^{-1})'] = (-\Delta H_o^{-1})' \times 10^3 - 0.03 [3 - (X_i^{-1})' \times 10^2]^2 - 18.3 = 0, \quad (17)$$

$\varphi_o > 0$: soft acids,

$\varphi_o < 0$: hard acids.

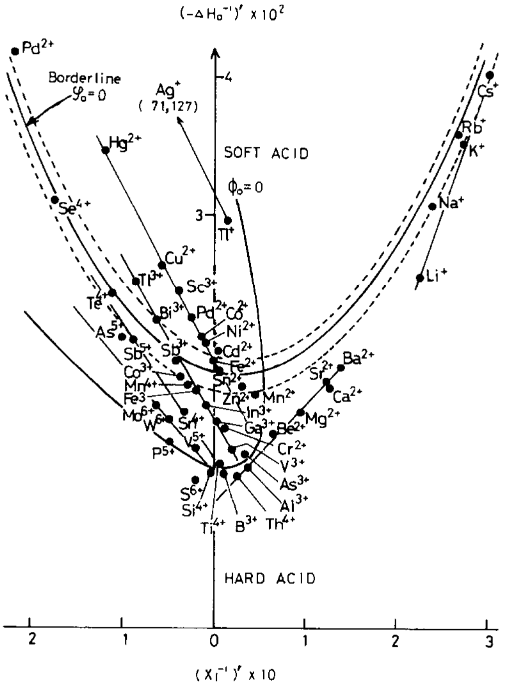

FIG. 4. Relation between $(-\Delta H_o^{-1})'$ and $(X_i^{-1})'$.

The relation between Z/r and X_i is plotted in Fig. 5. Metal oxides are divided into two kinds, oxidation catalysts and nonoxidation catalysts, by a border line expressed as

$$\phi_o(Z/r, X_i) = Z/r - 0.652\, X_i + 2.21 = 0, \quad (18)$$

$\phi_o(Z/r, X_i) < 0$: oxides having an oxidizing function,

$\phi_o(Z/r, X_i) > 0$: oxides having no oxidizing function.

The oxides are also classified into several groups depending on the acid–base property, much as in the case of $\phi(-\Delta H_o^{-1}, X_i^{-1})$ and $\Phi(\Sigma I_i/r, X_i^{-1})$.

On the other hand, the metal oxides may also be divided in another way, that is, as soft acids and hard acids, by a border line expressed as

$$\varphi_o(Z/r, X_i) = Z/r - 0.233\, X_i - 0.13 = 0, \quad (19)$$

$\varphi_o(Z/r, X_i) < 0$: soft acids,
$\varphi_o(Z/r, X_i) > 0$: hard acids.

The softness or hardness of various metal ionic acids was calculated on scales of $\varphi[(-\Delta H_o^{-1})', (X_i^{-1})']$ and $\varphi(Z/r, X_i)$ from the following two equations:

$$\varphi[(-\Delta H_o^{-1})', (X_i^{-1})'] = (-\Delta H_o^{-1})' \times 10^3 - 0.03 [3 - (X_i^{-1})' \times 10^2]^2 - 18.3 = 0, \quad (17')$$

$$\varphi(Z/r, X_i) = Z/r - 0.233\, X_i - 0.13 = 0. \quad (19')$$

The results are compared in Table 2 with the data which have previously been reported (*7, 8*).

TABLE 2

Soft–Hardness of Acid of Metal Ions

Ion (Group)[a]	$\varphi[(-\Delta H_o^{-1})', (X_i^{-1})']$	$\varphi(Z/r, X_i)$	Y^b	E^c	Soft–hard
Ag^+	−61.6	−0.67	3.99	−2.82	Soft acid
Tl^+	−11.28	−0.76	3.78	−1.88	
Hg^{2+}	−8.73	−0.50	4.24	−4.64	
Pd^{2+}	−7.99	−0.19	4.27	—	
Cu^{2+} (C)	−6.31	0.44	2.89	—	
Sc^{3+}	−4.38	1.47	—	—	
Pb^{2+}	−2.90	−0.66	3.58	—	
Tl^{3+}	−2.81	0.09	3.23	−3.37	
Co^{2+}	−1.73	0.47	2.96	−0.55	Borderline
Ni^{2+} (C)	−1.50	0.51	2.82	0.29	
Cd^{2+}	−1.42	−0.05	3.04	−2.04	
Zn^{2+} (B′)	−1.10	−0.41	2.34	—	
Bi^{3+} (B′)	−0.60	−0.45	—	—	
Fe^{2+}	−0.36	0.40	3.09	0.69	
Sn^{2+}	−0.12	−0.41	3.17	—	
Se^{4+}	0.10	—	—	—	
Te^{4+}	0.29	−0.04	—	—	
Rb^+	0.53	−0.01	—	—	
Sb^{3+}	1.09	0.03	—	—	
Co^{3+}	1.30	1.55	2.56	—	Hard acid
Cs^+ (D)	1.50	−0.03	2.73	—	
K^+ (D)	1.71	0.06	0.92	—	
Mn^{2+} (C)	1.77	0.68	3.03	—	
Na^+ (D)	1.84	0.29	0.93	—	
Mn^{4+} (C)	2.13	3.79	—	—	
Sb^{5+} (A)	2.36	3.07	—	—	
Ba^{2+} (D)	2.65	0.30	2.62	1.89	
Sr^{2+}	3.41	0.48	2.08	2.21	
In^{3+}	3.49	0.80	2.24	—	
As^{5+} (A′)	3.60	5.34	—	—	
Cr^{3+} (C)	3.61	1.86	2.70	—	
Ga^{3+}	3.92	2.16	—	1.45	
Fe^{3+} (B)	3.94	1.61	2.37	2.22	
Ca^{2+} (D)	3.98	0.72	1.62	2.33	
Mg^{2+} (D)	4.29	1.55	0.87	2.42	
Sn^{4+} (B)	4.29	1.74	—	—	
Li^+	4.01	0.84	0.36	0.49	
Be^{2+}	4.94	4.54	—	3.75	
Mo^{6+} (A)	4.98	4.10	—	—	
W^{6+} (A)	5.44	3.42	—	—	
V^{3+}	5.45	1.88	—	—	
As^{3+}	6.20	1.82	—	—	
P^{5+} (A′)	6.44	8.86	—	—	
Al^{3+} (A′)	6.70	3.42	0.70	6.01	
Ti^{4+} (B)	6.79	2.62	—	4.35	
Zr^{4+}	7.25	2.46	—	—	
B^{3+} (A′)	7.38	11.6	—	—	
Si^{4+}	7.42	5.94	—	—	
Th^{4+}	7.80	3.28	—	—	
V^{5+} (A)	8.17	4.25	—	—	
U_3O_8 (B)	8.48	(2.44)	—	—	
S^{6+} (A′)	8.87	12.3	—	—	

[a] Classification of metal oxides according to Ref. (1).
[b] Ref. (7).
[c] Ref. (8).

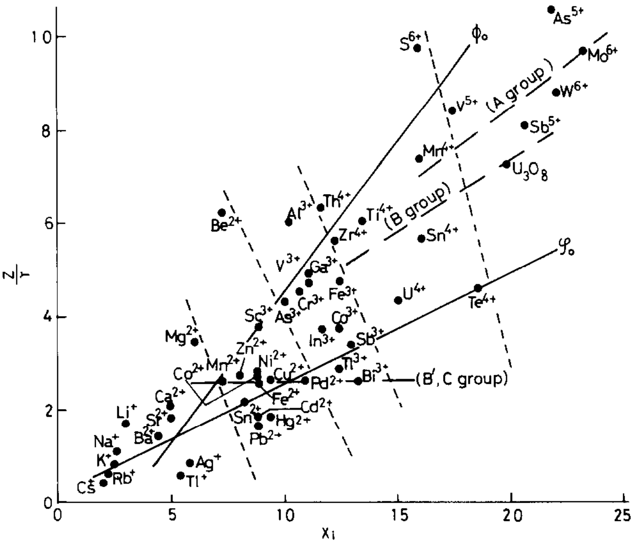

FIG. 5. Relation between Z/r and X_i.

The soft–hard border line, $\varphi_o = 0$, is also described in Figs. 1 and 3.

DISCUSSION

All the phenomena concerning chemical bonds are closely related to the movement of valence electrons, and this movement can be described approximately by the Hartree–Fock equation, especially as improved by Salter (*9*). The equation indicates that the energy of valence electrons consists of four parts: (i) the electrostatic energy of the force field of the nucleus, (ii) the electrostatic energy of the force field among other electrons, (iii) the exchange energy between the valence electrons and others, and (iv) the kinetic energy of the valence electrons. The potential energies of valence electrons, i.e., (i), (ii), and (iii), should be divided into two types: (i) and (ii) are the electrostatic potential energy, $Ve(r)$, and (iii) is the exchange potential energy.

It is better to express all phenomena relating to valence electrons in terms of these two types of energy. The action of an oxidation catalyst is, naturally, not an exception. The electrostatic energy of the nucleus on the surface is, possibly, reflected by Z/r; that is, the $Ve(r)$ may be approximated by Z/r. Similarly, the heat of formation of metal oxide $(-\Delta H_o)$, which is mainly associated with electrostatic energy, may also reflect the $Ve(r)$. On the other hand, the exchange energy is connected with the ionization potential and the electronic affinity of two atoms; therefore, the exchange energy can be approximated by electronegativity.

As the electronegativity, several scales have been proposed and the presence of correlations among them has also been pointed out. For convenience, the scale of Tanaka *et al.* was used in this study; however, the same correlations as Figs. 1 to 5 and Tables 1 and 2 may be obtained with the oxygen charge or electronegativity according to Sanderson's electronegativity equalization principle (*10*). The presence of a good correlation between Sanderson's and Tanaka's scales has also been reported by Tanaka (*11*).

In this study, it is demonstrated that numerous metal oxides can be classified in terms of several types of ϕ-functions which consist of the two different above-mentioned parameters. It is believed that this approach is better than past attempts, though it is still in a semiempirical and semiquantitative state.

This study will be followed by a second paper in which the application of the ϕ-functions to the oxidation activity of metal oxide catalysts is shown.

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