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Author(s)	NOTOYA, R.; MATSUDA, A.; KHODAKOV, Yu. S. et al.
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RELATIONSHIP BETWEEN ELECTRON ACCEPTABILITY OF MONOATOMIC CATIONS IN SOLVATION AND CATALYTIC ACTIVITY OF THEIR OXIDES

By

R. NOTOYA*), A. MATSUDA*), Yu. S. KHODAKOV**)
and Kh. M. MINACHEV**)

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The solvation bonding of monoatomic cations can be explained based upon the donor-acceptor nature of the ion-solvent interaction which is expressed by eq. (1)[1,2]

$$\frac{\alpha^0_{i,s}}{z_i} = \varepsilon_i \cdot \rho_s \tag{1}$$

$\alpha^0_{i,s}$ is the standard chemical free energy of solvation of monoatomic cation i of the valency z_i in solvent s. ρ_s is the electron donor strength of the solvent. It is defined as the gradient of the linear relation between $\alpha^0_{i,s}/z_i$ and the ionization energy I_i/z_i of ion i in the gas phase. ε_i is the electron acceptability of the ion. It can be related to I_i/z_i, as follows[2],

$$\varepsilon_i = \frac{I_i}{z_i} \tag{2}$$

for the cations of the rare gas type, the lanthanides and the actinides classified previously as (a)-group. For the cations classified as (b)-group which have more than three d-electrons in the outer shell, it can be expressed as

$$\varepsilon_i = 0.936\left(\frac{I_i}{z_i} - 0.93\right), \quad \text{eV}. \tag{3}$$

Finally for the cations of the electronic configuration of $5d^{10}+4f^{14}$ type classified as (c)-group, it is given by

$$\varepsilon_i = 0.862\left(\frac{I_i}{z_i} - 1.42\right), \quad \text{eV}. \tag{4}$$

The numerical representation of ρ_s for 15 solvents and ε_i for 78 ionic species was given in the previous work.[2]

On the other hand, many attempts have been made to interpret activity in catalysis

*) Research Institute for Catalysis, Hokkaido University, Sapporo, 060 Japan.
**) Institute of Organic Chemistry of Academy of Sciences of the USSR, Leninsky Prospekt, 47, Moscow, USSR.

by an approach based upon coordination chemistry, particularly for metal oxides.[3~5] Recently some prognostic rules for activity of metal oxides have been reported in the hydrogenation and double bond migration reactions of olefins and the dehydrogenation of hydrocarbons and the homomolecular hydrogen exchange.[6] These rules are summarized as 1) the activity of metal oxides increases with decreasing valency of the metal ion (Table 1), 2) the activity of metal oxides of elements in the same subgroup of the periodic table increases downward from the top to the bottom (Table 2).

It is interesting to compare the electron acceptability of a cation with the activity of the oxides of the ion in above 4 reactions. Fig. 1 shows the relation between the

TABLE 1. The dependence of catalytic activity of metal oxides on the valency of cations

The order of catalytic activity

$WO_2>WO_3$	$Cu_2O>CuO$
$V_2O_3>V_2O_5$	$Ce_2O_3>CeO_2$
$MnO>MnO_2$	$Tb_2O_3>Tb_4O_7$
$CrO>Cr_2O_3>CrO_3$	$MoO_2>MoO_3$

TABLE 2. The catalytic activity series of oxides of elements in the same subgroup of the periodic table for 4 reactions in the text

Subgroup	The order of catalytic activity
II a	BaO, $SrO>CaO>MgO$
III a	$La_2O_3>Y_2O_3>Sc_2O_3$
	$ThO_2>CeO_2$
III b	$Ga_2O_3>Al_2O_3$
IV a	$HfO_2>ZrO_2>TiO_2$
VI a	$WO_3>MoO_3>CrO_3$

TABLE 3. The catalytic activity series of oxides of elements in the same period of the periodic table for the homomolecular hydrogen exchange reaction

Period	The order of catalytic activity
3	$MgO>Al_2O_3>SiO_2$
4	$CaO>Sc_2O_3>TiO_2>V_2O_5$
5	$SrO>ZrO_2$, Nb_2O_5
6	$BaO>HfO_2>Ta_2O_5$

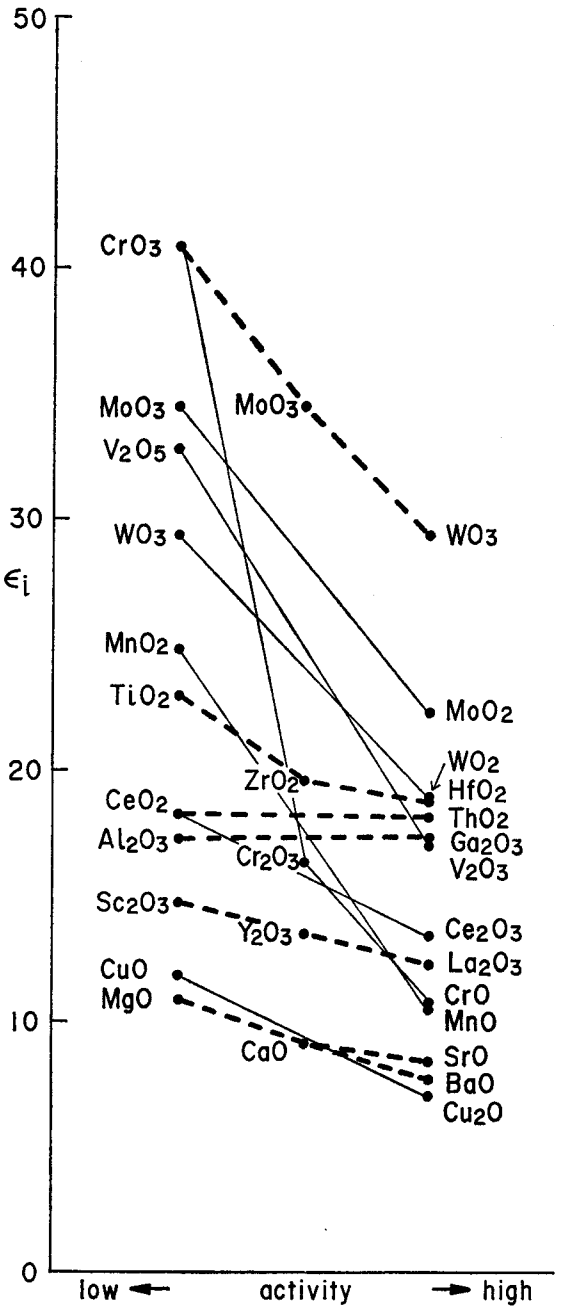

Fig. 1. The relation between the electron acceptability ε_i of cations and the catalytic activity of their oxides; —— for rule 1 and - - - - for rule 2.

values of ε_1 of cations and the activity of metal oxides in a qualitative manner. It is found that rules (1) and (2) can simply be expressed as: the activity of metal oxides in the above reactions increases with an decrease of the value of ε_1.

Khodakov and Minachev[6] have reported one more rule for the homomolecular exchange of hydrogen: the activity of metal oxides of elements in the same period of the periodic table increases in the direction from the right to the left, as shown in Table 3. This rule may also be explained by the fact that the values of ε_1 of ions of the elements in the same period decrease in the direction from the right to the left.

The relationship between ε_1 and the activity in catalysis will be discussed more extensively in a later work.

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