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EFFECT OF ELECTRONIC STRUCTURE AND TOLERANCE FACTOR ON CO OXIDATION ACTIVITY OF PEROVSKITE OXIDES

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CO oxidation was studied over perovskite-type compounds which were prepared by a conventional ceramic method. Catalytic activity strongly correlates both with the electronic state and the binding energy of transition metal in accordance with a tolerance factor of the perovskite structure.

Recently, perovskite oxides(ABO_3) have attracted considerable attention as redox catalysts for automobile exhaust treatments. It has been known that the CO oxidation activity of the perovskite catalysts is strongly affected by the variation of transition metal ions(1). Voorhoeve et al.(2) have indicated that the catalytic activity for the oxidation of CO is closely related with the electronic state of surface oxide ion. Furthermore, the electric properties of perovskite-type oxides are mainly determined by the electronic configuration of transition metal ion.

However, the information connected with the activity of CO oxidation has not been obtained from the tolerance factor which plays a crucial role in the crystallization of perovskite structure. In this letter, the relation will be discussed between the tolerance factor of various perovskite oxides, or the binding energy of oxide ions and the catalytic activity of CO oxidation.

Metals in La-metal perovskite oxides with the perovskite structure employed in this work are Ti, Ni, Fe, Mn and Co. Catalysts were prepared by a conventional ceramic method, using $La(OH)_3$ and carbonates of these metals or metal oxides as starting materials. In these compounds, La-Ni perovskite oxide was calcined using Na_2CO_3 as a flux. The products were analyzed by X-ray diffraction method and confirmed as a compound with the perovskite structure. There was evidence of single phase oxide from X-ray patterns, except La-Ti compound which was the mixture of pyroclore and perovskite phase. The surface areas of La-metal (Fe:2.08, Co:1.80, Ti:2.15, Ni:2.02, Mn:1.90 m^2/g) perovskite oxides were determined by Kr adsorption at liquid nitrogen temperature (BET method).

The perovskite structure is defined in terms of a tolerance factor: $t=(r_A+r_O)/\sqrt{2}(r_B+r_O)$ where r_A, r_B and r_O are the ionic radii of the metals A, B and oxygen. The radius of B ion, for a given A ion, is restricted by $0.7< t \leq 1.0$. Actually the perovskite structure is stable in this range.

The following equation as fomulated by Voorhoeve et al.(2) was employed to estimate the binding energy of oxygen which coordinates to the metal ions in various perovskite oxides.

$$(\text{ metal-O}) = \frac{1}{C_n \cdot m}\left(H_f - H_s \cdot m - \frac{n}{2} D_O\right) \qquad [1]$$

where H_f, H_s, D_O and C_n are the enthalpy of formation on one mole of oxide Me_mO_n, the sublimation energy of metal, the dissociation energy of O_2 and the coordination number of metal ions, respectively. The values of (A-O)+(B-O) for the various

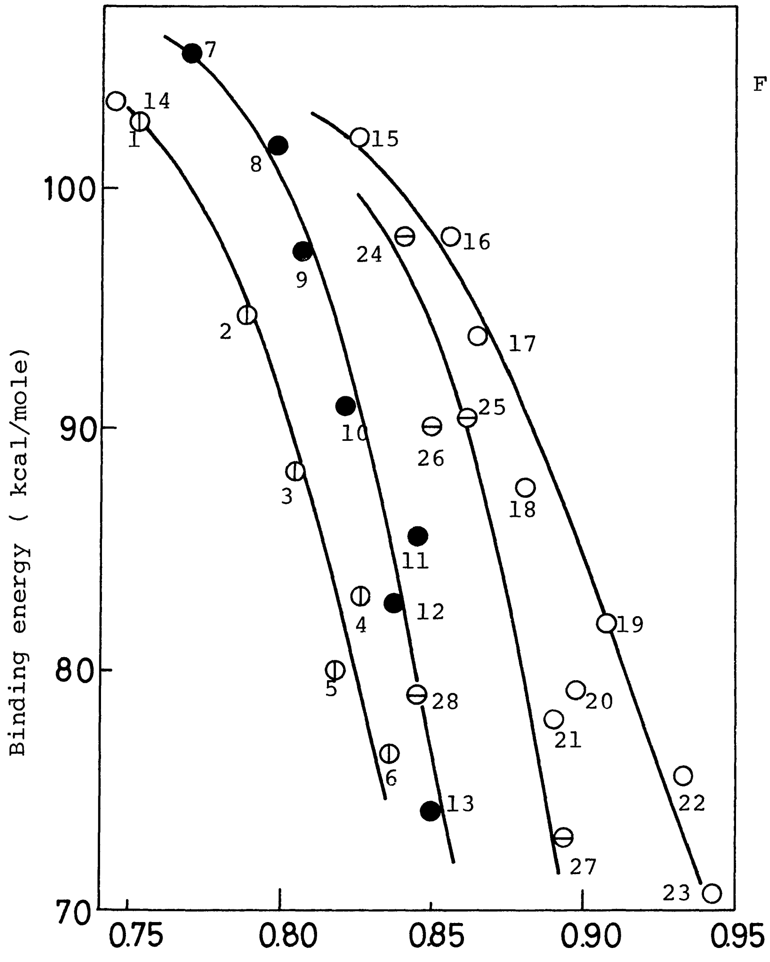

Fig.1 Binding energies calculated by Eq.1 versus "tolerance factor" of perovskite oxide (ABO_3).

Number in figure show the following perovskite oxide:

1; $YScO_3$, 2; YVO_3, 3; $YCrO_3$,
4; $YFeO_3$, 5; $YMnO_3$, 6; $YNiO_3$,
7; $GdScO_3$, 8; $GdTiO_3$,
9; $GdVO_3$, 10; $GdCrO_3$,
11; $GdFeO_3$, 12; $GdMnO_3$,
13; $GdCoO_3$, 14; $LaYO_3$,
15; $LaScO_3$, 16; $LaTiO_3$,
17; $LaVO_3$, 18; $LaCrO_3$,
19; $LaFeO_3$, 20; $LaMnO_3$,
21; $LaRhO_3$, 22; $LaNiO_3$,
23; $LaCoO_3$, 24; $CaTiO_3$,
25; $CaCrO_3$, 26; $CaVO_3$,
27; $CaMnO_3$, 28; $CaRuO_3$,

perovskite oxides were calculated from equation [1] and shown in Fig.1 as a function of the tolerance factor. The binding energy, for a given A ions, is decreased linearly with the increase of the tolerance factor. Using linear variations in Fig.1, we can immediately obtain the binding energy from the radius of the metal ion of perovskite oxides.

By definition, the tolerance factor increases with the decrease of the radius of transition metal ion. Accordingly, the increase of the tolerance factor will lower the interactions of B-O-B bond and may promote the formation of oxygen vacancies at the surface. Thus, it is plausible that the decrease of interactions in B-O-B bond causes considerable effects on the activity of CO oxidation. Oxides having the lower binding energy, therefore, have been used as the catalyst which is expected to be more active for CO oxidation.

The binding energy of La-perovskite oxides and the catalytic activity as the reciprocal temperature at which the activity is 5×10^{-5} mole CO m^{-2} min^{-1} are plotted in Fig.2 with Voorhoeve's data(3) as a function of the electronic occupation in the

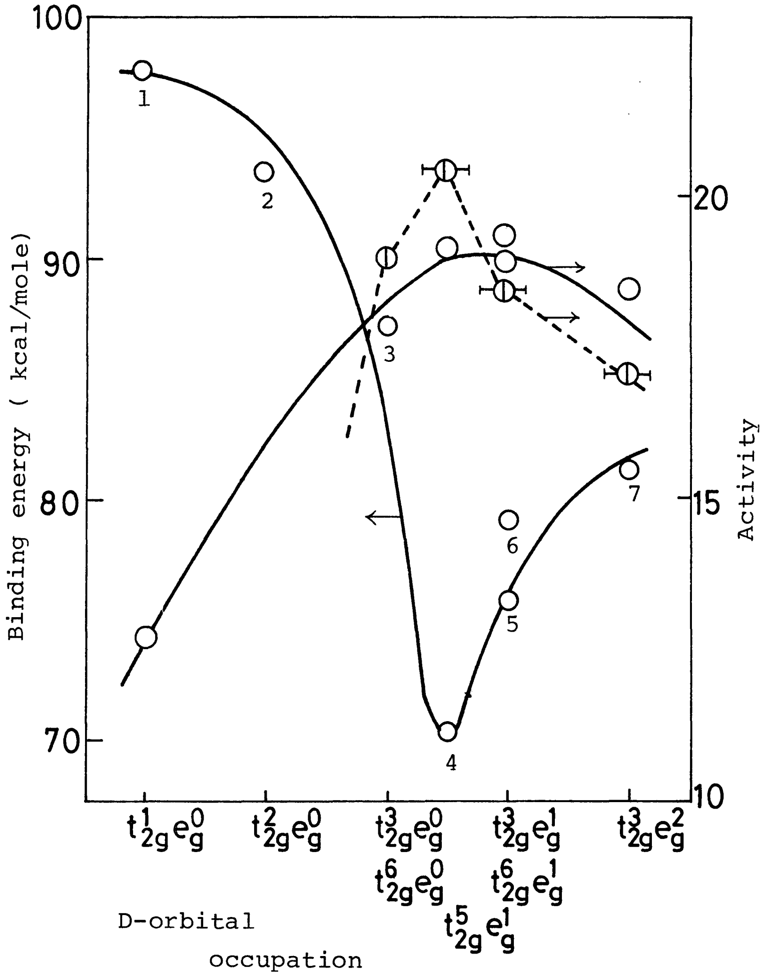

Fig.2 Binding energy and activity of La-metal perovskite catalysts versus the electric configuration of transition metal B ion.

Activity(○: our data, ⦶: Voorhoeve's data) is expressed as $10^4/T$, where T is the temp. at which the rate of CO oxidation is 5×10^{-5}mole CO·m^{-2} min^{-1} (○) and 10^{-6} mole CO·m^{-2} sec^{-1} (⦶).

Perovskite oxides:

1; $LaTiO_3$, 2; $LaVO_3$,
3; $LaCrO_3$, 4; $LaCoO_3$,
5; $LaNiO_3$, 6; $LaMnO_3$,
7; $LaFeO_3$,

t_{2g} and e_g levels of the transition metal ion according to Goodenough's classification method(4). It is obvious from Fig.2 that the decrease in the binding energy well corresponds to the increase of catalytic activity. The catalytic activity gives a maximum value at the minimum binding energy, or under the electronic configuration of e_g^x in the range $0 \leq x \leq 1$ and drops with an increase of the binding energy, or the occupation of e_g levels.

These results indicate that the binding energy of oxygen is an important factor in determination of the activity of CO oxidation. Furthermore, the catalytic activity is determined by both the symmetry and energy of d-orbitals of transition metal ion. It should be noted that the transition of electron spin to the empty e_g levels which form the lowest antibonding d-orbitals at the surface(5) plays an important role in the catalytic activity. The possibility of the chemisorption of CO to the surface in CO oxidation is suggested by these electronic phenomena and is agreement with the kinetic order of CO oxidation(6). The release of lattice oxygen, that is, the formation of oxygen vacancyies which resulted in the decrease of the binding energy, will be advantageous for the formation of adsorption site of oxygen which is brought about by the desorption of CO_2.

Fig.1 and Fig.2 are considered to be strong tools for selecting more active catalysts for CO oxidation and/or complete oxidation of hydrocarbons from various perovskite oxides.

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