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A New Hypothesis Regarding the Surface Acidity of Binary Metal Oxides[1]

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We have proposed a new hypothesis that the acid sites on binary metal oxides are formed by an excess of a negative or positive charge in the mixed oxides and that whether the charge is excess or not, and whether it is positive or negative, are determined by the coordination numbers and valences of the positive and negative elements in the model structures pictured according to two postulates. The validity of the hypothesis is, in fact, 90% for the 31 kinds of binary oxides tested, much higher than the validity (48%) of Thomas' hypothesis. The hypothesis explains well the mechanism of the acidity generation of binary oxides and predicts whether the acid sites will be of the Brönsted or the Lewis type.

Binary metal oxides, such as SiO_2–Al_2O_3, SiO_2–MgO, SiO_2–ZrO_2, and Al_2O_3–B_2O_3, are well-known to have surface acidity and have been used as solid acid catalysts for a long time.[2] It was only very recently, though, that TiO_2–ZnO,[3] SiO_2–ZnO,[4] SiO_2–TiO_2,[5] TiO_2–ZrO_2,[6,7] ZnO–Bi_2O_3,[7] Al_2O_3–MgO[7] *etc.* have been found to show an acidic property. Thus, many other binary metal oxides may also be expected to exhibit an acidic property. However, no one can predict what kinds of binary oxides will show an acidic property. An old but popular hypothesis proposed by Thomas,[8] which gave an interpretation of the acidity generation of five species of binary oxides that were known in 1949, has been found to fail in explaining the acidity generation of recently-found binary oxides. Therefore, we have developed a new hypothesis which is well applicable to many new kinds of binary oxides.

The Hypothesis

The acidity generation of binary oxides can generally be explained by the present hypothesis that the acidity generation is caused by an excess of a negative or positive charge in a model structure of a binary oxide. The model structure is pictured according to the following two postulates:

i) The coordination number of a positive element of a metal oxide, C_1, and that of a second metal oxide, C_2, are maintained even when mixed.

ii) The coordination number of a negative element (oxygen) of a major component oxide is retained for all the oxygens in a binary oxide.

For example, the structure of TiO_2–SiO_2, where TiO_2 is the major component oxide, and that of SiO_2–TiO_2, where SiO_2 is the major component oxide, are shown in Figs. 1a and 1b. In Figs. 1a and 1b, the coordination numbers of the positive elements in the component single oxides remain 4 for Si and 6 for Ti when they are mixed, whereas those of the negative elements should be 3 and 2 respectively, according to Postulates i) and ii). In the case of Fig. 1a, the four positive charges of the silicon atom are distributed to four bonds, *i.e.*, a positive charge is distributed to each bond, while the two negative charges of oxygen atom are distributed to three bonds, *i.e.*, $-2/3$ of a valence unit is distributed to each bond. The difference in charge for one bond is $+1-2/3=+1/3$, and for all the bonds the valence unit of $+1/3\times4=+4/3$ is excess. In this case, the Lewis acidity is assumed to appear upon the presence of an excess of the positive charge. In Fig. 1b, four positive charges of the titanium atom are distributed to six bonds, *i.e.*, $+4/6$ of a valence unit to each bond, while two negative charges of the oxygen atom are distributed to two bonds, *i.e.*, a negative charge to each bond. The charge difference for each bond is $+4/6-1=-1/3$, and for all the bonds the valence unit of $-1/3\times6=-2$ is excess. In this case, the Brönsted acidity is assumed to appear, because two protons are considered to associate with six oxygens to keep the electric neutrality. In any case, TiO_2–SiO_2 is expected to show an acidic property because of the excess of a positive or negative charge. In fact, it exhibited a very high acidity.[5]

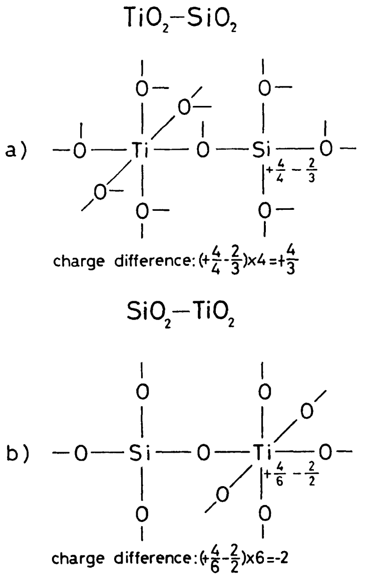

Fig. 1. Model structures of TiO_2–SiO_2 pictured according to postulates i) and ii). a): when TiO_2 is major oxide, b): when SiO_2 is major oxide.

Let us examine another example. In ZnO–Sb_2O_3, there is no excess charge in any part of its composition according to our model structure written by Postulates

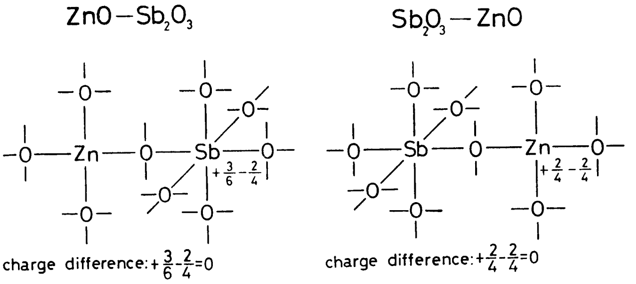

Fig. 2. Model structure of ZnO–Sb_2O_3 pictured according to postulates i) and ii). a): when ZnO is major oxide, b): when Sb_2O_3 is major oxide.

i) and ii), as is illustrated in Fig. 2. Therefore, the binary oxide is not expected to show any acidic property. This prediction agreed with an experimental result that ZnO–Sb_2O_3 did not show any acidity larger than the sum of the acidities of the component oxides.[7]

The Validity of the Hypothesis

The validity of our hypothesis was examined for 31 kinds of binary oxides. The case where the hypothesis predicts that a binary oxide should generate acidity is marked by an open circle in the fifth column of Table 1. On the other hand, the case where a binary oxide should not generate acidity is shown by a cross in the same column. The experimental results cited from the literature are shown in the next column, where open circles mark when the acid amount at a certain acid strength per unit surface area of any binary oxides is larger than the sum of the acid amounts at the same acid strength divided by the sum of the surface areas of the component single oxides, while crosses mark when no acidity is generated. The results indicate that new acid sites which differ from those of single oxides are created on the surface of 25 species of binary

Table 1. Validity of hypotheses
V: valence of positive element, C: coordniation number of positive element

Mixed-Oxides 1 2	$\alpha=V/C$ α_1	α_2	Acidity increase: Hypotheses: Thomas	Ours	Experimental results	No. of references	Validity of hypotheses: Thomas	Ours
TiO_2–CuO	4/6	2/4	×	○	○	10	×	○
TiO_2–MgO		2/6	○	○	○	7	○	○
TiO_2–ZnO		2/4	×	○	○	3	×	○
TiO_2–CdO		2/6	○	○	○	7	○	○
TiO_2–Al_2O_3		3/6	○	○	○	7	○	○
TiO_2–SiO_2		4/4	×	○	○	5,7	×	○
TiO_2–ZrO_2		4/8	×	○	○	6,7	×	○
TiO_2–PbO		2/8	×	○	○	10	×	○
TiO_2–Bi_2O_3		3/6	○	○	○	7	○	○
TiO_2–Fe_2O_3		3/6	○	○	○	10	○	○
ZnO–MgO	2/4	2/6	×	○	○	7	×	○
ZnO–Al_2O_3		3/6	×	×	○	7	×	×
ZnO–SiO_2		4/4	○	○	○	7	○	○
ZnO–ZrO_2		4/8	○	×	×	7	×	○
ZnO–PbO		2/8	○	○	×	7	×	×
ZnO–Sb_2O_3		3/6	×	×	×	7	○	○
ZnO–Bi_2O_3		3/6	×	×	×	7	○	○
Al_2O_3–MgO	3/6	2/6	○	○	○	10	○	○
Al_2O_3–B_2O_3		3/3	○	○	○	11	○	○
Al_2O_3–ZrO_2		4/8	×	×	○	7	×	×
Al_2O_3–Sb_2O_3		3/6	×	×	×	7	○	○
Al_2O_3–Bi_2O_3		3/6	×	×	×	7	○	○
SiO_2–BeO	4/4	2/4	○	○	○	12	○	○
SiO_2–MgO		2/6	×	○	○	13,14	×	○
SiO_2–CaO		2/6	×	○	○	15	×	○
SiO_2–SrO		2/6	×	○	?	15	?	?
SiO_2–BaO		2/6	×	○	?	15	?	?
SiO_2–Ga_2O_3		3/6	×	○	○	12	×	○
SiO_2–Al_2O_3		3/4,3/6	○	○	○	14	○	○
SiO_2–Y_2O_3		3/6	×	○	○	12	×	○
SiO_2–La_2O_3		3/6	×	○	○	12	×	○
SiO_2–ZrO_2		4/8	○	○	○	14	○	○
ZrO_2–CdO	4/8	2/6	×	○	○	7	×	○

Thomas' hypothesis 15/31=48%
Our hypothesis 28/31=90%

oxides. Cases where the result predicted by the hypothesis agrees with the experimental result is marked by open circles in the last column of Table 1, and cases of disagreement, by a cross. As may be seen in the table, an agreement of the prediction of our hypothesis with the experimental results was found for 28 of the 31 kinds of binary oxides. Thus, the validity of our hypothesis is 90%.

Thomas[8] proposed that the acidities of binary oxides are generated when $C_1=C_2$ and $V_1<V_2$ or when $C_1=2C_2$, where C_1 and C_2 are the coordination numbers of a positive element and a second one and where V_1 and V_2 are the valences of the respective positive elements. The validity of his hypothesis is only 48%, as is shown in Table 1. Therefore, it has been verified that our hypothesis is much better. It should also be noted that the validity of his hypothesis is low despite the fact that the coordination number of oxygen is taken as arbitrary so as to fit the experimental results.

The binary oxides which are predicted to generate surface acidity according to our hypothesis, but not according to Thomas' hypothesis, are the following thirteen species: TiO_2–CuO, TiO_2–ZnO, TiO_2–SiO_2, TiO_2–ZrO_2, TiO_2–PbO, ZnO–MgO, ZnO–ZrO_2, SiO_2–MgO, SiO_2–CaO, SiO_2–Ga_2O_3, SiO_2–Y_2O_3, SiO_2–La_2O_3, and ZrO_2–CdO. It was verified by experiments that all of the binary oxides showed a distinct acidity increase. In particular, TiO_2–SiO_2 showed a higher acidity and catalytic activity than the well-known SiO_2–Al_2O_3 catalyst.[5] TiO_2–ZnO, whose acidity was much higher than that of each component oxide, showed a surprisingly high activity for the hydration of ethylene.[3]

Though Thomas' hypothesis cannot be applied to Lewis acids,[8] our hypothesis also predicts the type of acid sites (Brönsted or Lewis), as has been mentioned above. According to our hypothesis, TiO_2–ZnO should show Brönsted acidity when TiO_2 is a major component oxide and Lewis acidity when ZnO is a major component oxide. An infrared study of pyridine adsorbed on the binary oxide revealed that TiO_2 including 5% of ZnO exhibited Brönsted acidity alone, while ZnO including 5% of TiO_2 exhibited Lewis acidity alone.[3]

Limitations of the Hypothesis

As may be seen in the model structures (Figs. 1 and 2) pictured according to Postulates i) and ii), the present hypothesis is applicable to chemically-mixed binary oxides, but not to mechanically-mixed oxides. Since the binary oxides given in Table 1 were prepared by calcining mixtures of co-precipitated hydroxides at a high temperature (500 °C), they are not mechanically-mixed oxides. The X-ray diffraction diagrams of the binary oxides showed no or weak diffraction lines, and almost all of them were assumed to be amorphous.[3,6,7,10] Thus, the structures are different from those of the component single oxides.

The present hypothesis predicts which combinations of oxides in the periodic table will generate acidity and at what compositions the Brönsted or Lewis acidity will appear, but it does not predict the acid strength. The prediction of the acid strength was reported in a foregoing paper,[7] which demonstrated a good correlation between the acid strength and the average electronegativities of metal ions of binary oxides, though the prediction is not based on any hypothesis, but on a generalization.

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