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# The Acidity and Basicity of $Bi_2O_3$-based Binary Oxides

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The numbers of both acidic and basic sites in a series of $Bi_2O_3$–$X_nO_m$ binary oxides, with different kinds and amounts of the second component, $X_nO_m$, were systematically determined by means of the adsorption of $NH_3$ and $CO_2$ from the gas phase, using the static method. Pure $Bi_2O_3$ has both acidic and basic sites, much like $TiO_2$, $SnO_2$, and $Fe_2O_3$, and it is more basic than these oxides. The generation of an unexpectedly high acidity or basicity was not observed in the combination of $Bi_2O_3$ with 11 kinds of oxides, and the acid-base properties of the binary oxides can be understood in terms of the nature of the second component. The order of ability for the promotion of the acidity and the diminution of the basicity is: $MoO_3$, $SO_3$, $WO_3 > V_2O_5$, $P_2O_5 > Sb_2O_4 > TiO_2$, $SnO_2$, $Fe_2O_3$. The addition of $K_2O$ decreases the acidity and increases the basicity. The relationship between the acid-base properties and the catalytic activities for the isomerization of 1-butene, the dehydration and dehydrogenation of 2-propanol, and the oxidative decomposition of formic acid was investigated. It was proposed that the basic sites of the $Bi_2O_3$-based mixed oxides originate from $Bi_2O_3$ and that the nature remains approximately the same, regardless of any change in the kind and amount of the second component. However, the acidic sites are generated by the combination with second component; therefore, the nature varies widely depending on the nature of the second component.

Recently, it has been proposed that acid-base-type interaction between the catalyst surface and the organic substance to be oxidized plays the determining role in mild oxidation, and that the combination of metal oxides contributes to a modification of the acid-base properties.[1–3] On this basis, it is of decisive importance to know the acid-base properties of the oxidation catalysts. However, there have been very few reports dealing with the acid-base properties of mixed transition-metal oxides.

The purpose of the present study is to determine systematically the acid-base properties of the $Bi_2O_3$–$X_nO_m$ (where $X_nO_m$ consists of different kinds and amounts of oxides) binary system and to demonstrate how the incorporation of foreign oxides into $Bi_2O_3$ modifies the acid-base properties.

## Experimental

*Catalysts.* The catalysts used in this study were a series of $Bi_2O_3$–$X_nO_m$ with different X/Bi ratios (X/Bi= 0—1.0), where $X_nO_m$ refers to 11 different kinds. They were prepared as follows. The required quantities of bismuth nitrate were dissolved in concentrated nitric acid, and to this was added an aqueous solution or a slurry of the second metallic component; thereafter, 10- to 20-mesh pumice (surface area$<$0.3 m$^2$/g) originating from volcanic rocks was mixed with the solution, and the mixture was evaporated with vigorous stirring. The amount of pumice was 500 ml in a stream of oxygen at 500 °C for 4 to 5 h. As the starting materials, the following compounds were used: nitrate for Fe; ammonium salts of oxy acids for V, Mo, and W; chlorides (converted to hydroxides by dilute ammonia) for Ti and Sn; hydrate for K; $H_2SO_4$ for S; $H_3PO_4$ for P; and Sb powder (converted to oxide by concentrated nitric acid) for Sb. The surface areas were measured by the BET method using nitrogen at −196 °C.

*Acidity and Basicity Measurements.* Since the $Bi_2O_3$-based oxides are colored, the determination of the acidity and basicity by an ordinary titration method[4] seems to be difficult; therefore, it was attempted to measure the acidity and basicity by means of the adsorption of the basic and acidic molecules respectively from the gas phase, using the static method.[5–7] $NH_3$ and $CO_2$ were chosen as the adsorbates. The amount of adsorption at a pressure of 300 mmHg was measured volumetrically using an ordinary BET apparatus. Subsequently, the catalyst was pumped out for 30 min at the same temperature. Then, similar adsorption procedures were repeated and the amount of readsorption was measured. The amount of irreversible adsorption was obtained as the difference between the amount of readsorption and that of the first adsorption. This was adopted as the measure of the acidity and basicity. The details of the procedures were the same as those described in the previous papers.[5–7]

*Catalytic Activity Measurements.* The dehydration and dehydrogenation of 2-propanol (IPA), the isomerization of 1-butene, and the oxidative decomposition of formic acid were carried out in an ordinary continuous-flow system. The reactor was a steel tube, 50 cm in length and 1.8 cm in internal diameter. It was immersed in a lead bath, the temperature of which was controlled within ±1 °C. The concentrations of 2-propanol, 1-butene, and formic acid were 1.65, 0.67, and 1.2 mol% in air respectively. The total flow rate was kept constant at 1.5 l/min (at 25 °C), and the amount of catalyst used weighed 1 to 20 g. The details of the experimental procedures were the same as those employed in the previous works.[5–7]

## Results

*Acidity.* The acidity (number of acidic site) per unit of the surface area of the $Bi_2O_3$–$X_nO_m$ catalysts, as determined by the amount of $NH_3$ irreversibly adsorbed at 200 °C, is plotted as a function of the $X_nO_m$ content in Figs. 1 and 2.

The acidity of pure $Bi_2O_3$ is relatively low. The acidity increases markedly upon the incorporation of acidic compounds. The order of this promoting ability is found to be: $SO_3 > MoO_3 > WO_3 > P_2O_5 > V_2O_5 > Sb_2O_4$. The abilities of amphoteric oxides such as $SnO_2$, $TiO_2$, $Al_2O_3$, and $Fe_2O_3$ are less prominent. The acidic sites are extinguished by the addition of a small amount of $K_2O$.

*Basicity.* The basicity (number of basic site) per unit of the surface area of the $Bi_2O_3$–$X_nO_m$ catalysts, as

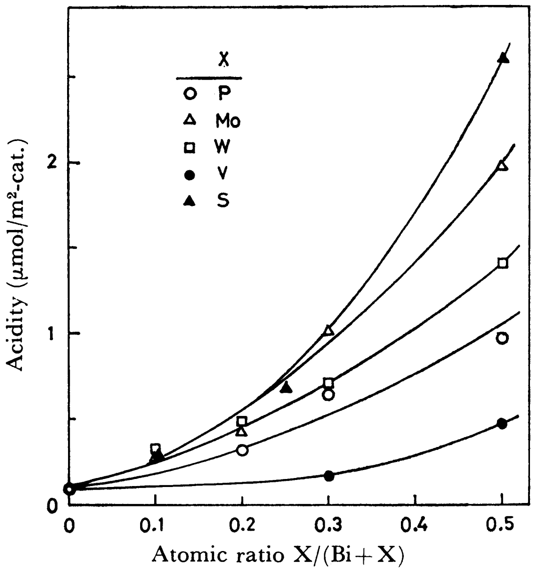

Fig. 1. Acidity of $Bi_2O_3$-$X_nO_m$ (I).

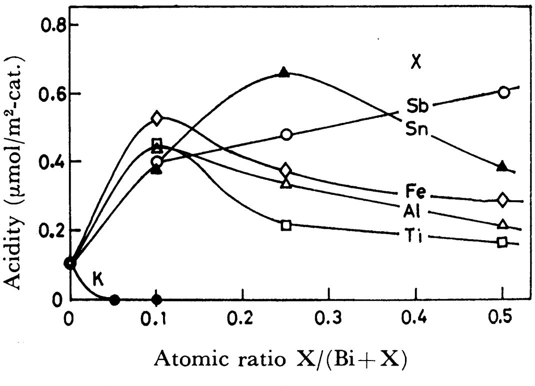

Fig. 2. Acidity of $Bi_2O_3$-$X_nO_m$ (II).

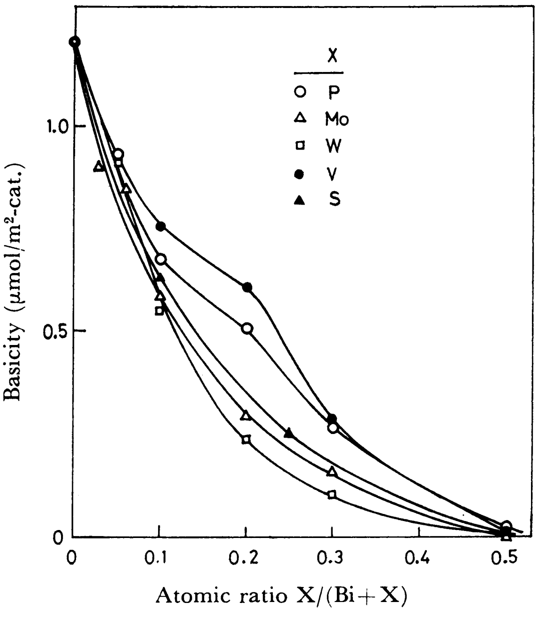

Fig. 3. Basicity of $Bi_2O_3$-$X_nO_m$ (I).

determined by the amount of $CO_2$ irreversibly adsorbed at 25 °C, is plotted in Figs. 3 and 4.

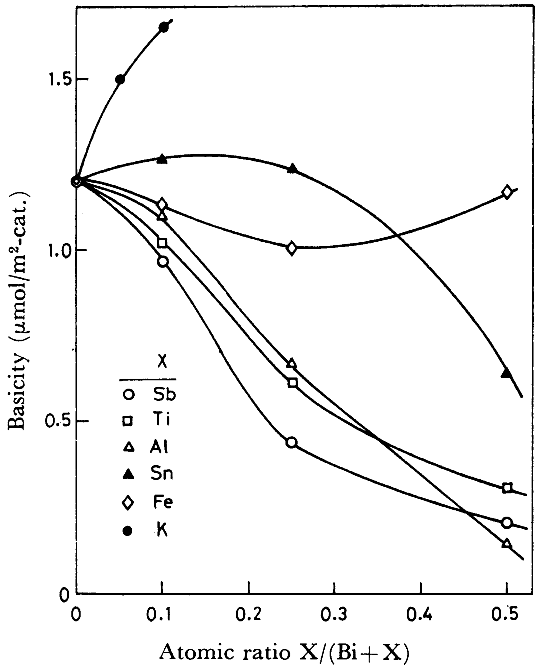

Fig. 4. Basicity of $Bi_2O_3$-$X_nO_m$ (II).

$Bi_2O_3$ by itself is fairly basic. The basicity decreases upon the addition of more acidic compounds. The ability to diminish basicity is found to be in this order: $WO_3 > MoO_3 > SO_3 > V_2O_5 = P_2O_5 > Sb_2O_4 > TiO_2 = Al_2O_3 > SnO_2$. The ability of $Fe_2O_3$ is small, and the addition of $K_2O$ increases the basicity.

*Correlation between Acidity and Catalytic Activity.* In order to confirm the validity of the acidity data, their correlation with the catalytic activity for certain acid-catalyzed reactions was checked. The dehydration of 2-propanol to propylene and the isomerization of 1-butene to 2-butenes were chosen as the model reactions, since it has been shown with various kinds of mixed metal oxides that the catalytic activity for the two reactions, as measured in a continuous-flow experiment in an atmosphere of air, can be tied with the acidity.[1,5–8]

*Dehydration Activity for 2-Propanol*: A gaseous mixture of 2-propanol and air was passed through a bed of the catalyst under the above-mentioned conditions. The main products were propylene and acetone, and the amounts of the other products were negligibly small. The rate of dehydration at 242 °C, $r_p$ (mole per hour $m^2$ of catalyst), was measured for certain binary systems with relatively high acidities. Following the principle of the differential reactor, the conversion was held at a slow level, *i.e.*, usually below 10%.

The results are plotted in Fig. 5 as a function of the acidity of the catalysts. It is found that, so long as the second component, $X_nO_m$, is the same, the values of $r_p$ vary in the same direction as the acidity.

*Isomerization Activity for Butene*: The activity for the isomerization of 1-butene to 2-butenes under the circumstances of the oxidation reaction at 473 °C, $r_i$ (mole per hour $m^2$ of catalyst), was studied for certain binary systems with relatively high acidities.[1,6–8]

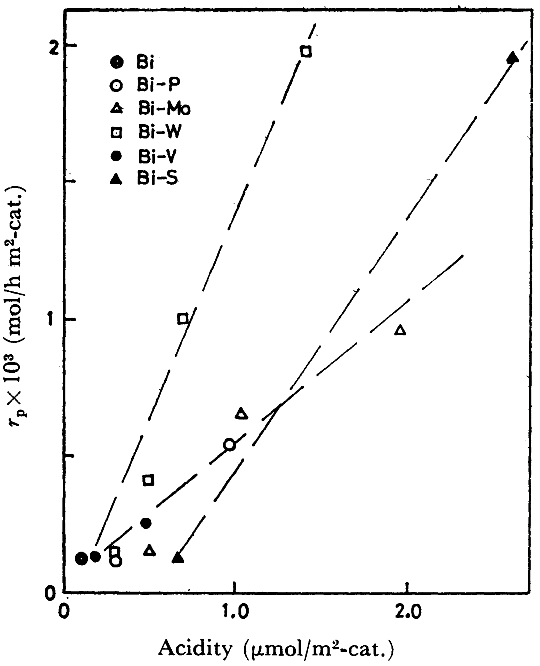

Fig. 5. Relation between the dehydration activity for 2-propanol at 242 °C ($r_p$) and the acidity of catalyst.

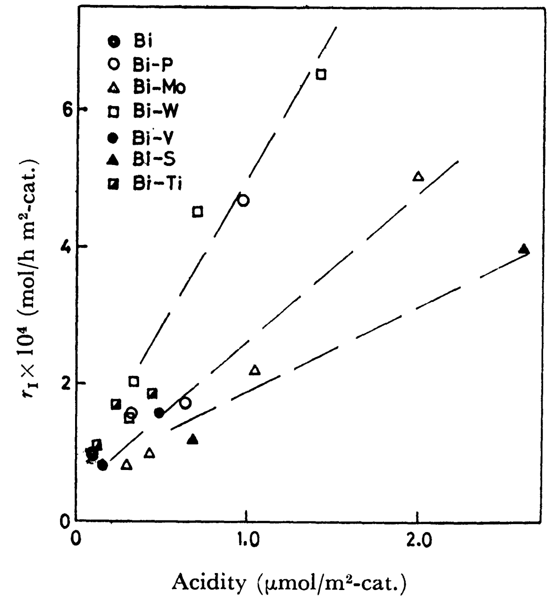

Fig. 6. Relation between the isomerization activity for 1-butene at 473 °C ($r_I$) and the acidity of catalyst.

It is plotted in Fig. 6 as a function of the acidity of the catalysts. Much as with the dehydration activity for 2-propanol, the isomerization activity changes in the same direction as the acidity, so long as the second component, $X_nO_m$, is the same.

*Correlation between Basicity and Catalytic Activity.* Next, the basicity data were confirmed by studying the correlation with the catalytic activity for certain base-catalyzed reactions. It has been shown that the catalytic activity for the oxidative decomposition of formic acid to $CO_2$[8] and the $r_a/r_p$ ratio, where $r_p$ and $r_a$ are the initial rates of 2-propanol dehydration and dehydrogenation respectively,[1,6,9] are effective as measures of the basicity of the oxidation catalysts.

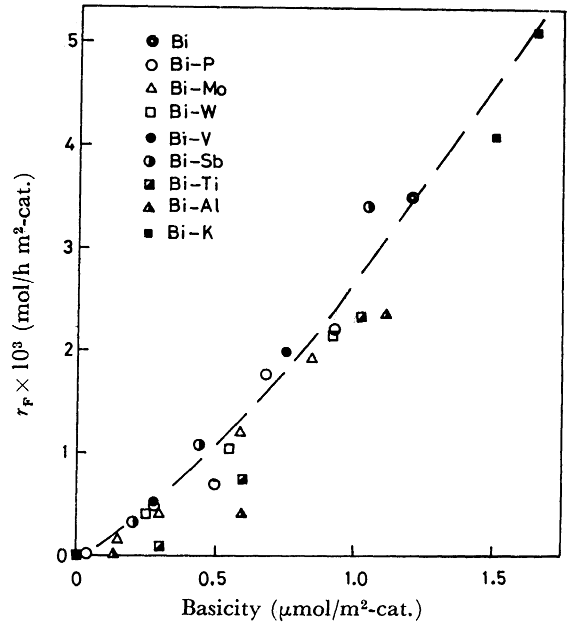

Fig. 7. Relation between the activity for oxidative decomposition of formic acid to $CO_2$ 155 °C ($r_F$) and the basicity of catalyst.

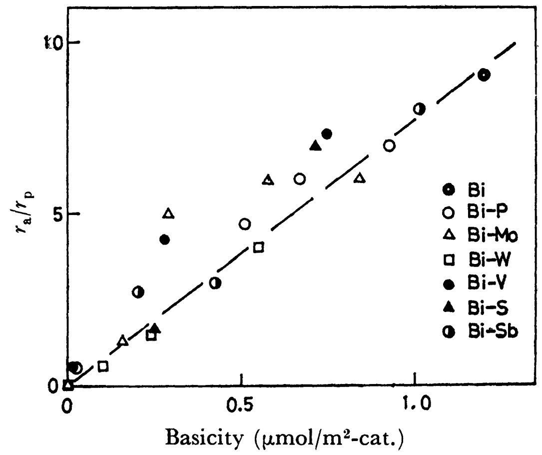

Fig. 8. Relation between the $r_a/r_p$ ration and the basicity of catalyst.

*Oxidative Decomposition of Formic Acid*: As has been mentioned in a previous paper,[8] the reaction products were $CO_2$ and $H_2O$, and the amounts of CO and $H_2$ were negligibly small. The rate of $CO_2$ formation at 115 °C, $r_F$ (mole per hour m² of catalyst), was measured for each catalyst. It is plotted in Fig. 7 as a function of the basicity of the catalysts. A very good correlation is observed between the activity and the basicity.

*(Dehydrogenation Activity)/(Dehydration Activity) Ratio in the Reaction of 2-Propanol*: The $r_a/r_p$ ratio is plotted in Fig. 8 as a function of the basicity. A relatively good correlation is obtained between the $r_a/r_p$ ratio and the basicity.

## Discussion

It was found that $Bi_2O_3$ by itself has both acidic and basic sites, much like $TiO_2$, $SnO_2$, and $Fe_2O_3$, and that $Bi_2O_3$ is more basic than the latter oxides; this is in conformity with the earlier results.[6,7,9–11] It was also demonstrated in a direct way that the $Bi_2O_3$-based mixed oxides are, more or less, acid-base bifunctional and that the generation of an unexpectedly high acidity or basicity, which often occurs in combination of metal oxides, was not observed. Therefore, the acid-base properties can be understood relatively easily in terms of the nature of the second components, $X_nO_m$.[1,2,9] The more acidic the second component, the more acidic and the less basic become the binary oxides. The order of the ability to promote acidity and diminish basicity is found to be: $MoO_3$, $SO_3$, $WO_3 > V_2O_5$, $P_2O_5 > Sb_2O_4 > TiO_2$, $SnO_2$, $Fe_2O_3$. The effect of the amphoteric oxides, such as $TiO_2$, $SnO_2$, $Fe_2O_3$, and $Al_2O_3$, is less prominent. Contrary to the acidic compounds, the addition of $K_2O$ decreases the acidity and increases the basicity. In the case of oxidation catalysts, the valence of metal is varied by the combination of oxides, so it seems difficult to predict the acidity generation basing on the hypothesis proposed by Tanabe *et al.*[12]

We would like to propose the following view. When $Bi_2O_3$ is combined with a more acidic oxide, the basic sites of the mixed oxides originate from $Bi_2O_3$ and some of the basic sites are extinguished by the combination of the acidic compound, as can be reasonably expected in the case of a liquid acid-base. Accordingly, the natures of the basic sites remain approximately the same, regardless of the changes in kind and amount of the second component, $X_nO_m$. This may be the main reason why the plots of the activity for base-catalyzed reactions against the basicity give a straight line extraporated through the point of origin.

On the other hand, the acidic sites of the binary oxides do not originate from $Bi_2O_3$ but are generated by the combination with second components. Consequently, the natures of the acidic sites vary widely depending on the nature of the second components, $X_nO_m$. This may be the reason why the correlation between the catalytic activity and the acidity is obtained only when the second component is of the same kind.

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