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The Relationship between the Oxidation Activity and the Acid–Base Properties of Fe_2O_3-Based Mixed Oxides

II. The Fe_2O_3–P_2O_5, Fe_2O_3–K_2O, and Fe_2O_3–Bi_2O_3–P_2O_5 Systems

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Both the acidity and basicity of Fe_2O_3–P_2O_5 and Fe_2O_3–K_2O, with different compositions, were directly measured by means of the adsorption of NH_3, pyridine, CO_2, and SO_2 from the gas phase. With the addition of P_2O_5 or K_2O, the acid–base properties of the Fe_2O_3-based catalysts vary as can be expected from the natures of P_2O_5 and K_2O. The acidic character of Fe_2O_3–P_2O_5 is fairly low compared with that of Fe_2O_3–V_2O_5 and Fe_2O_3–MoO_3. The acidity data were confirmed by the catalytic activities for acid-catalyzed reactions such as isomerization of 1-butene and dehydration of isopropyl alcohol. Then, the acid–base properties of a series of ternary oxides, Fe_2O_3–Bi_2O_3–P_2O_5, with different Bi/Fe compositions and a constant P_2O_5 content, $P/(Fe + Bi) = 1/10$, were also determined. The Bi_2O_3–P_2O_5 ($P/Bi = 1/10$) is far more basic and less acidic than the Fe_2O_3–P_2O_5 ($P/Fe = 1/10$). With the substitution of Bi_2O_3 for Fe_2O_3, the acidity of the mixed oxides decreases and the basicity increases steadily. The vapor-phase oxidation of *n*-hexane, 1-butene, butadiene, methanol, and formic acid was carried out in an ordinary continuous-flow reactor. Then, the relationship between the catalytic behavior and the acid–base properties of the catalysts was investigated. The results support an earlier proposal that the oxidation activity and selectivity can be interpreted in terms of the acid–base properties of the metal oxide catalysts and the reactants.

INTRODUCTION

We have studied selective oxidations on the basis of an idea that the combination of metal oxides contributes to a modification in the acid–base properties and that this modification induces a change in the catalytic functions (*1*).

The present paper is the second part of an investigation on the oxidation activity of Fe_2O_3-based mixed oxide catalysts. In the preceding paper (*2*) the Fe_2O_3–V_2O_5 and Fe_2O_3–MoO_3 systems were studied. It was found that the catalytic activity and selectivity in the oxidation of olefins, which change remarkably with the composition, can be interpreted in terms of the acid–base properties of the binary oxides.

In this work, Fe_2O_3 was combined with an oxide which by itself has no oxidizing function, such as P_2O_5 and K_2O. Next iron in the Fe_2O_3–P_2O_5 ($P/Fe = \frac{1}{10}$) was replaced progressively by bismuth. We attempted to confirm whether or not the change in the oxidation activity and selectivity can be interpreted by the change in the acid–base properties.

EXPERIMENTAL METHODS

The catalysts used in this study were two series of binary oxides, Fe_2O_3–P_2O_5 and Fe_2O_3–K_2O, with different composi-

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tions, and a series of ternary oxides, Fe_2O_3–Bi_2O_3–P_2O_5, with eleven different Bi/Fe ratios and a constant phosphorus content, $[P/(Fe + Bi) = \frac{1}{10}]$. As the starting materials, $Fe(NO_3)_3 \cdot 9H_2O$, 85 wt% H_3PO_4, KOH, and $Bi(NO_3)_3 \cdot 5H_2O$ were used. They were prepared by the procedures described in the preceding paper (*2*).

The acidity and basicity of the catalysts were measured by means of the adsorption of basic and acidic molecules, respectively, from the gas phase, using either the static or pulse method. The technique of the measurements has been described in earlier papers (*2–5*).

The vapor-phase oxidation of 1-butene, butadiene, *n*-hexane, and methanol, the isomerization of 1-butene, the dehydration of isopropyl alcohol (IPA), and the oxidative decomposition of formic acid were carried out in an ordinary continuous-flow system. The reactor and the experimental and analytical procedures were the same as those employed in the earlier works (*2–5*).

RESULTS

1. Surface Area

First, the effect of the composition on the specific surface area was checked by the BET method, using nitrogen at −196°C. The results are shown in Tables 1 and 2. The surface area increases gradually with the P_2O_5 content and reaches a maximum at P = 10 at%, while the effect of the K_2O addition is small. In the case of the Fe_2O_3–Bi_2O_3–P_2O_5 system, a striking decrease in the surface area occurs when 30 to 50 at% of iron is replaced by bismuth.

TABLE 1

Surface Areas of the Fe_2O_3–P_2O_5 and Fe_2O_3–K_2O Catalysts

Composition P/(Fe + P)	Surface area (m^2/g)	Composition K/(Fe + K)	Surface area (m^2/g)
0	9.8	0	9.8
0.01	11.8	0.005	9.8
0.02	16.0	0.01	9.2
0.05	28.5	0.02	9.4
0.10	33.2	0.03	9.1
0.15	31.4	0.04	8.6
0.20	23.2	0.05	9.1
0.30	22.4	0.07	8.1
0.40	18.4		

TABLE 2

Surface Areas of the Fe_2O_3–Bi_2O_3–P_2O_5 Catalysts

Composition[a] Bi/(Fe + Bi)	Surface area (m^2/g)	Composition[a] Bi/(Fe + Bi)	Surface area (m^2/g)
0	29.2	0.33	3.6
0.03	29.0	0.50	1.5
0.06	29.4	0.67	1.9
0.10	24.4	0.85	1.4
0.15	20.5	1.00	1.8
0.20	17.0		

[a] P/(Fe + Bi) = 0.10.

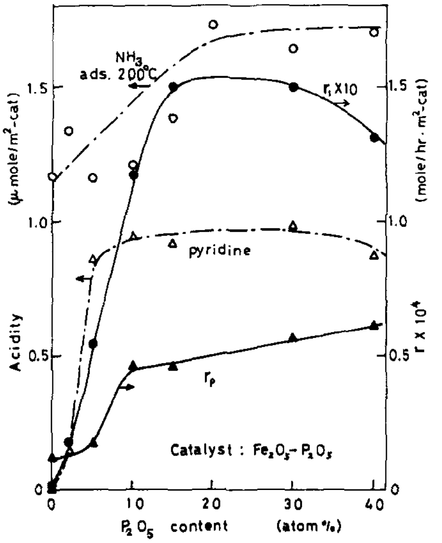

FIG. 1. Acidity of Fe_2O_3–P_2O_5 as a function of the P_2O_5 content: (○) irreversible adsorption of NH_3 at 200°C; (△) pyridine required to poison the isomerization activity for 1-butene at 230°C; (▲) the dehydration activity for IPA at 218°C, r_p; (●) the isomerization activity for 1-butene at 300°C, r_i.

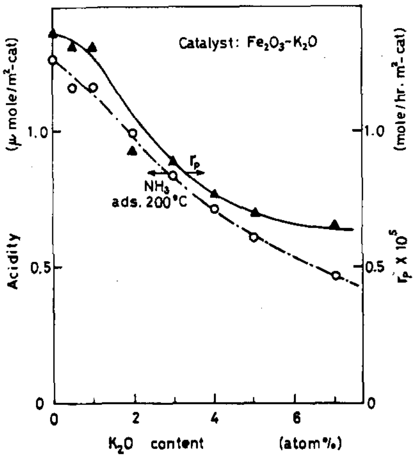

FIG. 2. Acidity of Fe_2O_3–K_2O as a function of the K_2O content: (○) irreversible adsorption of NH_3 at 200°C; (▲) the dehydration activity for IPA at 218°C, r_p.

2. Acidity

The acidity (number of acidic site) per unit of surface area of the catalysts, as determined by the amount of NH_3 irreversibly adsorbed at 200 or 240°C (static method) and by the amount of pyridine required to poison the isomerization activity for 1-butene at 230°C (pulse method), is plotted as a function of the catalyst composition in Figs. 1, 2, and 3.

In order to confirm the values of acidity, the catalytic activity for several acid-catalyzed reactions was investigated. The dehydration of IPA to propylene and the isomerization of 1-butene to 2-butenes, in the presence of an excess of air were chosen as the model reactions (*2*, *5*, *6*). They were carried out in a continuous-flow system. The concentrations of IPA and 1-butene were 1.33 and 1.0 mol% in air. The total flow rate (at 25°C) was kept constant at 1.0 liter/min and the amounts of the catalysts were 1 to 20 g. The initial rate of IPA dehydration at 218°C, r_p, and the rate of butene isomerization at 300°C, r_I (mole/hr·m² of catalyst), are plotted together with the values of acidity in Figs. 1 and 2. The values of r_p and r_I vary in the same direction as do those of acidity.

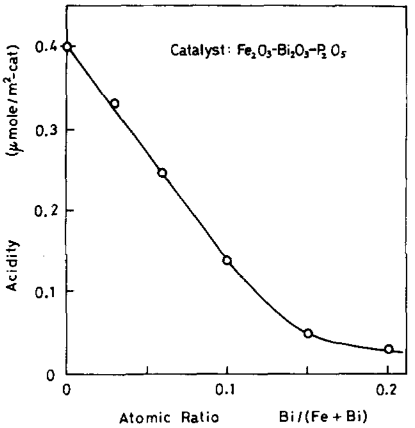

FIG. 3. Acidity of Fe_2O_3–Bi_2O_3–P_2O_5 as a function of the Bi/(Fe + Bi) ratio: P/(Fe + Bi) = $\frac{1}{10}$, acidity = irreversible adsorption of NH_3 at 240°C.

3. Basicity

The basicity (number of basic site) per unit of surface area of the catalysts, as determined by the amounts of CO_2 and SO_2 irreversibly adsorbed at 30 and 115°C, respectively (static method), is plotted as the function of the catalyst composition in Figs. 4, 5, and 6.

4. Intrinsic Oxidation Activity

Paraffinic hydrocarbons and hydrogen may act upon metal oxide catalysts, more or less, as electron-donating reagents. However, this tendency might be so weak that the activity for the combustion of these compounds is really governed by the intrinsic oxidation activity of the surface rather than by the activation of the reactant molecules (*3*, *7*, *8*). For convenience in the experimental procedures, combustion of *n*-hexane was chosen as a model reaction which reflects the intrinsic oxidation activity (*2*–*5*, *7*).

The reaction was carried out keeping the following conditions constant at T = 352°C, *n*-hexane = 0.4 mol% in air, and total flow rate = 1.0 liter/min, while

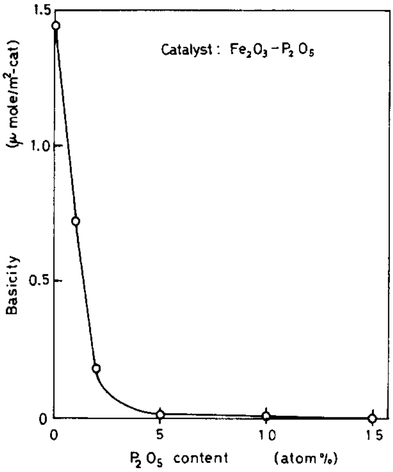

FIG. 4. Basicity of Fe_2O_3–P_2O_5 as a function of the P_2O_5 content: irreversible adsorption of CO_2 at 30°C.

the amounts of catalysts used were varied in the range of 1 to 20 g, in order to achieve a proper conversion. The initial rate of *n*-hexane oxidation to CO_2, r_H (mole/hr·m² of catalyst), was measured as an index of the activity. The results are plotted as a function of the basicity (the amount of adsorbed CO_2) of the Fe_2O_3–P_2O_5 in Fig. 7. It was found that the activity decreases steadily with a decrease in the basicity.

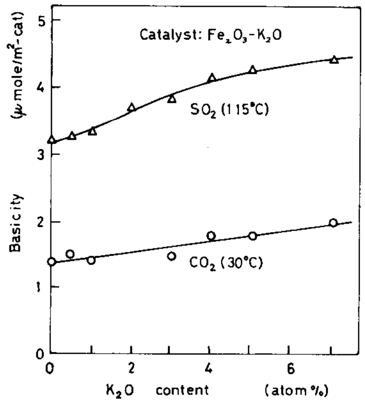

FIG. 5. Basicity of Fe_2O_3–K_2O as a function of the K_2O content: (○) irreversible adsorption of CO_2 at 30°C; (△) irreversible adsorption of SO_2 at 115°C.

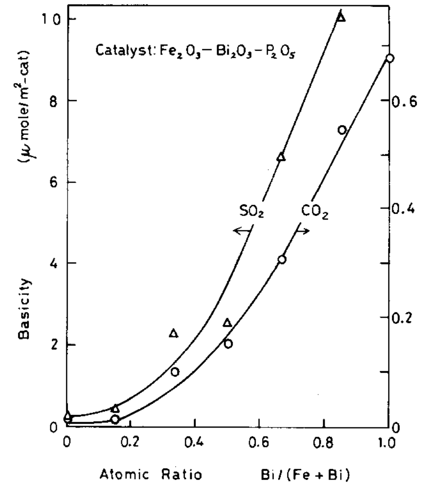

FIG. 6. Basicity of Fe_2O_3–Bi_2O_3–P_2O_5 as a function of the Bi/(Fe + Bi) ratio: P/(Fe + Bi) = $\frac{1}{10}$, (○) irreversible adsorption of CO_2 at 30°C; (△) irreversible adsorption of SO_2 at 115°C.

5. *Oxidation of 1-Butene*

The oxidation of 1-butene was carried out at the concentrations of $1-C_4H_8-O_2-N_2$ = 1.0–1.0–98.0 mol% or 1.0–1.3–97.7 mol% and the total flow rate of 1.0 liter/min, in the temperature range between 270 and 360°C. The amounts of catalysts were varied from 1 to 20 g, to achieve a proper

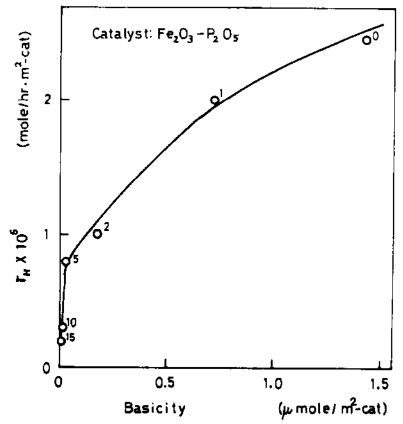

FIG. 7. Relation between the basicity of the Fe_2O_3–P_2O_5 catalysts and the oxidation activity for *n*-hexane. r_H: Rate of *n*-hexane oxidation to CO_2 (hexane base) at 352°C, n-C_6H_{14} = 0.4 mol% in air. Numbers correspond to the contents (atomic percent) of phosphorus in the Fe_2O_3–P_2O_5.

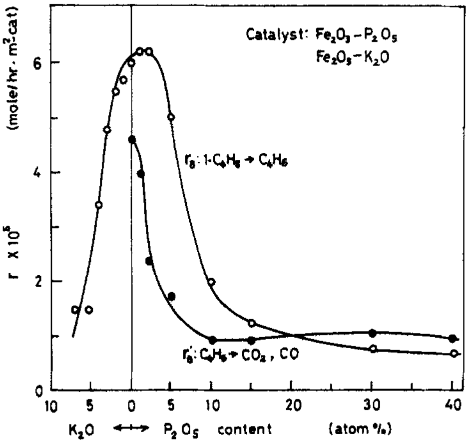

FIG. 8. Oxidation activities for 1-butene and butadiene as a function of the content of P_2O_5 or K_2O: r_B: Rate of 1-butene oxidation to butadiene at $T = 305°C$, $1\text{-}C_4H_8\text{-}O_2\text{-}N_2 = 1.0\text{-}1.0\text{-}98.0$ mol%; r'_B: rate of butadiene consumption at $T = 308°C$, $C_4H_6 = 1.0$ mol% in air.

conversion. The main products were butadiene, CO_2, and CO, and the amounts of the other products were very small. The initial rates of butadiene formation at 305°C for the Fe_2O_3–P_2O_5 and Fe_2O_3–K_2O catalysts and at 300°C for the Fe_2O_3–Bi_2O_3–P_2O_5 catalysts, r_B (mole/hr·m² of catalyst), were measured as an index of the activity for this reaction. The results are shown in Figs. 8 and 9.

With the addition of P_2O_5, the activity first increases up to a sharp maximum at P = 1 to 2 at% and then decreases. The activity decreases steadily as the K_2O content increases. In the case of the Fe_2O_3–Bi_2O_3–P_2O_5 system, the activity attains a maximum at Bi/(Fe + Bi) = 0.05.

The selectivity to butadiene at fixed total conversions is shown in Figs. 10 and 11. A maximum occurs in the selectivity, too.

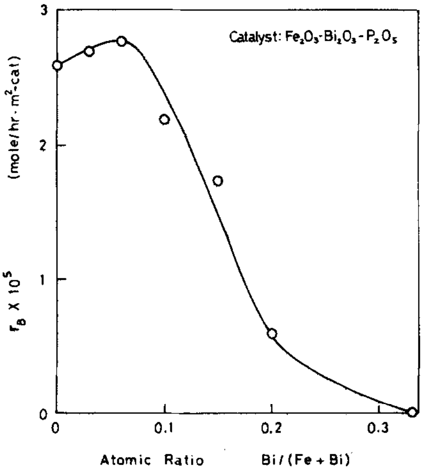

FIG. 9. Oxidation activity for 1-butene as a function of the Bi/(Fe + Bi) ratio: r_B: rate of 1-butene oxidation to butadiene at $T = 300°C$, $1\text{-}C_4H_8\text{-}O_2\text{-}N_2 = 1.0\text{-}1.3\text{-}97.7$ mol%.

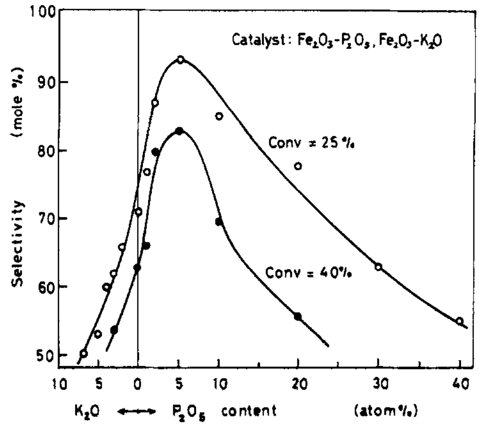

FIG. 10. Selectivity of 1-butene to butadiene as a function of the content of P_2O_5 or K_2O: $T = 300\text{–}350°C$, $1\text{-}C_4H_8\text{-}O_2\text{-}N_2 = 1.0\text{-}1.0\text{-}98.0$ mol%.

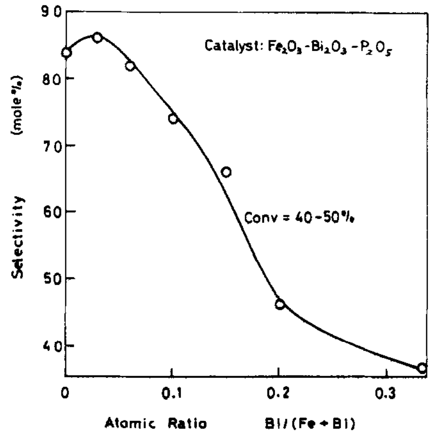

FIG. 11. Selectivity of 1-butene to butadiene as a function of the Bi/(Fe + Bi) ratio: $T = 270\text{–}360°C$, $1\text{-}C_4H_8\text{-}O_2\text{-}N_2 = 1.0\text{-}1.3\text{-}97.7$ mol%.

6. *Oxidation of Butadiene*

As a model of "acid-formation" reactions, the oxidation of butadiene to maleic anhydride was chosen in the same way as in the preceding work (*2*). The reaction was carried out at 300 to 420°C, the butadiene concentration of 1.0 mol% in air, and the total flow rate of 1.0 liter/min, using the catalysts in the range 1 to 20 g. The main products were only CO_2 and CO, and the amounts of maleic anhydride, acetic acid, and the other compounds were negligibly small, even when the P_2O_5 content were high, P = 30 to 40 at%. The initial rate of butadiene consumption at 308°C, $r'_{B'}$ (mole/hr·m² of catalyst), is plotted together with the activity for the oxidation of 1-butene to butadiene (r_B) in Fig. 8.

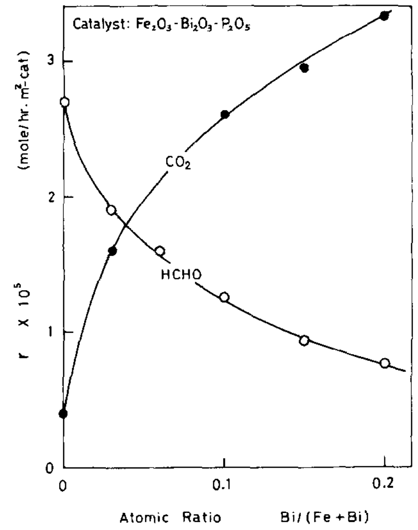

FIG. 13. Oxidation activity for methanol as a function of the Bi/(Fe + Bi) ratio: T = 265°C, CH_3OH = 2.6 mol% in air.

7. *Oxidation of Methanol*

Since Fe_2O_3–MoO_3 catalysts are known to exhibit an excellent selectivity in the oxidation of methanol to formaldehyde, the catalytic behavior of the Fe_2O_3–P_2O_5, Fe_2O_3–K_2O, and Fe_2O_3–Bi_2O_3–P_2O_5 for this reaction is tested.

The reaction was carried out at 265, 275, and 300°C, the methanol concentration of 2.6 mol% in air, and the total flow rate of 1.0 liter/min, by changing the amounts of catalysts in the range of 1 to 20 g. The main products were formaldehyde and CO_2, and the amounts of the other products were negligibly small. The initial rates of formaldehyde and CO_2 formation, r_F and r_{CO} (mole/hr·m² of catalyst), were measured following the principle of the differential reactor. The results are shown in Figs. 12, 13, and 14.

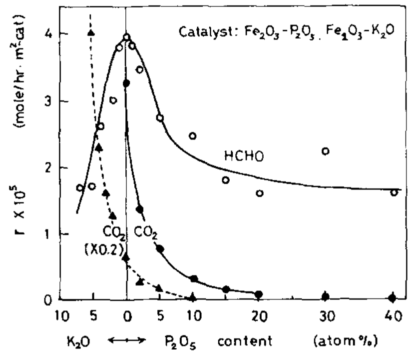

FIG. 12. Oxidation activity for methanol as a function of the content of P_2O_5 or K_2O: T = 275°C, CH_3OH = 2.6 mol% in air.

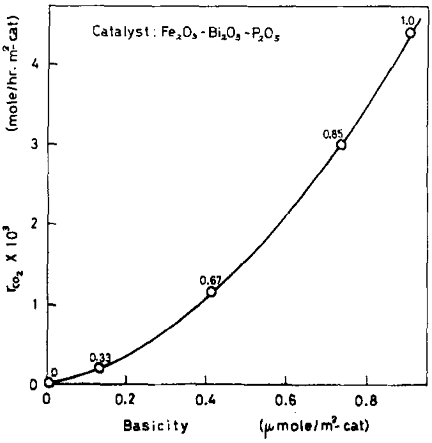

FIG. 14. Relation between the basicity of the Fe_2O_3–Bi_2O_3–P_2O_5 catalysts and the activity for oxidation of methanol to CO_2. r_{CO_2}: Rate of the CO_2 formation at T = 300°C, CH_3OH = 2.6 mol% in air. The numerals show the Bi/(Fe + Bi) ratios.

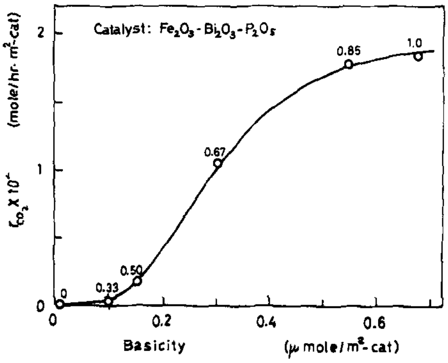

FIG. 15. Relation between the basicity of the Fe_2O_3–Bi_2O_3–P_2O_5 catalysts and the activity for oxidative decomposition of formic acid to CO_2. r_{CO_2}: Rate of the CO_2 formation at 204°C and HCOOH = 1.8 mol% in air. The numerals show the Bi/(Fe + Bi) ratios.

8. *Oxidative Decomposition of Formic Acid*

The activity for decomposition of formic acid was tested with the Fe_2O_3–Bi_2O_3–P_2O_5 catalysts. The reaction was carried out at 1.8 mol% HCOOH in air and at the total flow rate of 1.0 liter/min, by changing the amounts of catalysts from 1 to 20 g. The initial rates of CO_2 and CO formation at 204°C, r_{CO_2} and r_{CO} (mole/hr·m^2 of catalyst), were measured as indexes of the activities for each reaction. The results are plotted as a function of either the basicity or the acidity of the catalysts in Figs. 15 and 16.

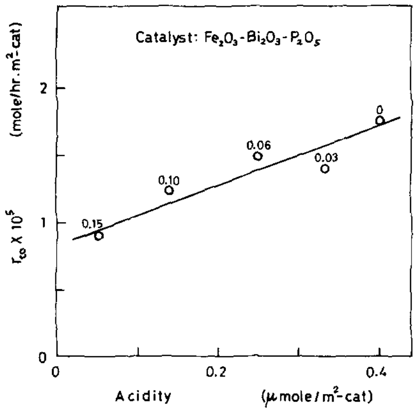

FIG. 16. Relation between the acidity of the Fe_2O_3–Bi_2O_3–P_2O_5 catalysts and the activity for decomposition of formic acid to CO. r_{CO}: Rate of the CO formation at 204°C and HCOOH = 1.8 mol% in air. The numerals show the Bi/(Fe + Bi) ratios.

DISCUSSION

As can be easily expected from the natures of P_2O_5 and K_2O, the acidity increases with an increase in the P_2O_5 content and it decreases with the K_2O content. In contrast, the basicity decreases rapidly with the P_2O_5 addition and it increases a little with the K_2O addition. However, it should be borne in mind that the acidic character of Fe_2O_3–P_2O_5 is fairly low compared with that of Fe_2O_3–V_2O_5 and Fe_2O_3–MoO_3 (*2*). This can also be seen from the fact that severe conditions, i.e., high temperatures, are required to achieve an appreciable conversion in the acid-catalyzed reactions with the Fe_2O_3–P_2O_5 catalysts compared with the Fe_2O_3–V_2O_5 and Fe_2O_3–MoO_3 catalysts (*2*).

The same phenomenon was observed in the case of SnO_2-based oxides (*9*). That is, SnO_2–V_2O_5 and SnO_2–MoO_3, especially at Sn/V < 70/30 and Sn/Mo = 70/30, are fairly acidic, while the acidic character of the SnO_2–P_2O_5 (P < 20 at%) is not eminent.

The fact that no acidic products can be obtained in the oxidation of butadiene with the Fe_2O_3–P_2O_5 catalysts can be understood from the acidic character. As has been pointed out earlier (*2*, *7*, *9*), a necessary condition for an effective catalyst in acid-formation reactions is the possession of a sufficient acidic property. That is, the Fe_2O_3–V_2O_5 and Fe_2O_3–MoO_3 are acidic enough to produce acidic compounds, but the Fe_2O_3–P_2O_5 catalysts are not sufficiently acidic. As a result, the produced acidic compounds are easily activated by the basic sites and reoxidized to CO_2 or CO. The SnO_2–P_2O_5 catalysts, much like the Fe_2O_3–P_2O_5, are not effective for the acid-formation reaction (*9*).

Though both Fe_2O_3 and Bi_2O_3 are acid–base bifunctional oxides, Bi_2O_3 is more basic and less acidic than Fe_2O_3 (*1*, *4*, *10*).

It should be noted that this brings about a striking difference between the Fe_2O_3–P_2O_5 and Bi_2O_3–P_2O_5. The outline of acid-base properties of the Fe_2O_3–Bi_2O_3–P_2O_5 ternary oxides can be understood from the natures of the two binary oxides combined. However, the shapes of the curves in Figs. 3 and 6 also indicate that the acidic sites of the Fe_2O_3–P_2O_5 are extinguished very rapidly by combination with a basic compound such as the Bi_2O_3–P_2O_5 and, in contrast, the basic sites of the Bi_2O_3–P_2O_5 are extinguished by the combination with an acidic compound such as the Fe_2O_3–P_2O_5, that is, a sort of neutralization occurs by the combination of the two binary oxides.

It is clear from Fig. 15 that the oxidative decomposition of formic acid to CO_2 is catalyzed by basic sites. It should be borne in mind that the Bi_2O_3-rich catalysts are remarkably active for this reaction, while the Fe_2O_3-rich catalysts are fairly inactive. On the other hand, Fig. 16 indicates that the activity for the decomposition of formic acid to CO decreases as the acidity decreases. The results are consistent with those obtained from many other oxide catalysts (*4*). This may indicate the validity of the acidity–basicity data shown in Figs. 3 and 6.

The results shown in Fig. 7 indicate that the intrinsic oxidation activity is dependent on the basicity of the catalysts. This finding is in accord with the results of the previous studies (*3*, *7*) and supports the view that the ability of catalyst to activate and to incorporate gaseous oxygen into the crystal-lattice oxygen (O^{2-}) by electron transfer from the metal oxide to the oxygen is connected with the basic property of the catalyst (*1–3*).

The oxidation activity for 1-butene increases a little with the addition of a small amount of P_2O_5 which by itself has no oxidizing functions (Fig. 8). However, the activity reaches a maximum at $P = 1$ to 2 at% and it decreases rapidly with a further addition of P_2O_5. The addition of K_2O reduces the activity. In the case of the Fe_2O_3–Bi_2O_3–P_2O_5 system, the activity also has a maximum (Fig. 9). Concerning the results, we would like to propose the following interpretation.

As has been mentioned in the preceding paper (*2*), the oxidation activity is generally governed by two functions: (i) activation of olefin on the acidic sites and (ii) activation of gaseous oxygen, which is connected with the basic character of the surface. It must be kept in mind that the Fe_2O_3–P_2O_5, unlike the Fe_2O_3–MoO_3, are not eminent in the acidic character and, as a result, their ability to activate olefin is not eminent. Therefore, the reaction requires the presence of relatively active oxygen. Thus, the activation of olefin by acidic sites is not the sole factor deciding the oxidation activity and the activity is affected, to a considerable extent, by the activation of oxygen on the basic sites.

When Fe_2O_3 is combined with K_2O, the catalysts are deficient in the acidic function for olefin activation and the activity is limited by this function, therefore, the activity decreases with a decrease in the acidity. On the other hand, when the content of P_2O_5 is high, the catalyst is deficient in the function for oxygen activation and the activity is limited by this function, therefore, the activity decreases with a decrease in the basicity. A maximum in the activity is obtained when acidic and basic properties of the catalysts are proper for the objected oxidation, for example, at $P = 1$ to 2 at%.

As mentioned above, the Fe_2O_3–P_2O_5 ($P/Fe = \frac{1}{10}$) is a little too acidic to be satisfactory for the reaction. Therefore, the acid–base properties proper to this reaction are achieved by the substitutions of Bi_2O_3 for Fe_2O_3 in the range of $Bi/(Fe + Bi) = 0.03$ to 0.05. The fairly low activity of the Bi_2O_3-rich catalysts, $Bi/(Fe + Bi) > 0.3$, is caused by their lack in the acidic character, i.e., the function for activation of butene.

The selectivity to butadiene increases upon the addition of a small amount of P_2O_5, much as in the case of the V_2O_5 or MoO_3 addition (*2*), and it reaches a maximum at P = 5 at%. The addition of K_2O decreases the selectivity (Fig. 10). The results can be explained according to the view (*7*, *9*) that a requirement for an effective catalyst in oxidation of a basic reactant to a basic product is the possession of a moderate character both in the acid and the base. Fe_2O_3 by itself is too basic to be satisfactory for these type reactions and the addition of about 5 at% phosphorus decreases the basic property and brings about the acid-base properties proper to this reaction.

As shown in Fig. 8, the Fe_2O_3-based oxides are fairly active for the oxidative degradation of butadiene and the activity of the Fe_2O_3–P_2O_5 system is related to the basicity rather than to the acidity.

The selectivity of the Fe_2O_3–Bi_2O_3–P_2O_5 catalysts (Fig. 11) can also be explained by the same view. As mentioned above, the Fe_2O_3–P_2O_5 ($P/Fe = \frac{1}{10}$) is too acidic with respect to the selectivity, too. The substitution of a small amount, [$Bi/(Fe + Bi) = 0.03$], of Bi_2O_3 for Fe_2O_3 decreases the acidic character and brings about the acid–base properties proper to the reaction.

With regard to the methanol oxidation, the activity to form CO_2 is correlated with the basicity of the catalysts (Figs. 12 and 14). This finding supports the view (*11*) that the CO_2 formation is catalyzed by the basic sites. In the case of the Fe_2O_3–Bi_2O_3–P_2O_5 catalysts, the activity for formaldehyde formation decreases as the acidity decreases (Fig. 13). The results are consistent with those obtained from many other oxide catalysts (*11*). However, in the case of the Fe_2O_3–P_2O_5 system, it is difficult to correlate the activity with the acidity. To explain the results, we would like to propose the following hypothesis that the formaldehyde by nature is fairly stable compared with methanol under the oxidation conditions and, therefore, a certain portion of methanol can be oxidized to formaldehyde even if the oxidation is effected without a sufficient activation of methanol by acidic sites.

At any event, the following principle is still valid that formaldehyde is the sole product as long as the catalysts are acidic enough and that the selectivity to formaldehyde decreases and the selectivity to CO_2 increases with an increase in the basic property.

It is demonstrated in this study that oxidation activity of a metal oxide catalyst is strikingly different as different nature of reactants. For example, the Fe_2O_3–P_2O_5 ($P/Fe = \frac{1}{10}$) is active for the oxidation of butene, while it is relatively inactive for the oxidation of formic acid and methanol. In contrast, the Bi_2O_3–P_2O_5 ($P/Bi = \frac{1}{10}$) is inactive for the butene oxidation, while it is extremely active for the complete oxidation of formic acid and methanol.

We would like to emphasize here that these findings can be well interpreted in terms of acid–base properties between the reactant molecule and the metal oxide, that is, a basic reactant such as olefin is activated by acidic sites and a reactant which can act as an acid is activated by basic sites.

It is concluded that the variation in the catalytic activity, induced by the modification of the catalyst composition, can be relatively well interpreted in terms of the acid–base properties of the catalysts. It is proposed here also that the combination of metal oxides contributes to the enhancement or modification of the acid–base properties.

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