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Activities for the Decomposition of Formic Acid and the Acid–Base Properties of Metal Oxide Catalysts

MAMORU AI

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan

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Studies have been made to ascertain whether the catalytic activity for the oxidative dehydrogenation of formic acid to CO_2 is effective as an index of the basicity of metal oxides, which are used as oxidation catalysts. The basicity of the catalysts was measured by means of the adsorption of CO_2 and of acetic acid and by titration with benzoic acid. The decomposition of formic acid was carried out in the presence of an excess of air using a continuous-flow reaction system, in order to obtain data for the valence states of the metal oxide which were at a steady state. With such basic oxides as SnO_2–K_2O, ZnO–K_2O, Bi_2O_3–K_2O, Bi_2O_3–MoO_3, and Bi_2O_3–P_2O_5, only the oxidative dehydrogenation to form CO_2 and H_2O takes place, and the catalytic activity for this reaction is well correlated with the basicity. With acidic oxides such as WO_3–P_2O_5, TiO_2–MoO_3, and SnO_2–MoO_3, only the dehydration to CO takes place, and the activity for this reaction is correlated with the acidity. Then, the catalytic activities for the dehydration and oxidative dehydrogenation were measured systematically using various kinds of single and mixed metal oxide catalysts. A clear regularity between the catalytic behavior of the metal oxides and their acid–base properties was found. It is concluded that, as an index of basicity of solid catalysts, the catalytic activity for the oxidative dehydrogenation of formic acid is effective for rather basic catalysts, while the (dehydrogenation activity for isopropyl alcohol, IPA)/(dehydration activity for IPA) ratio is valid for rather acidic catalysts.

INTRODUCTION

In previous papers (*1–4*), the present authors showed that the catalytic activity and selectivity of metal oxides in mild oxidations are associated with the acid–base properties between catalysts and reactants. However, it is not always easy to determine the acid–base properties of oxidation catalysts by the ordinary titration method (*5–7*) or by studying the adsorption of a basic or acidic molecule from the gas phase (*8–10*), because the oxidation catalysts, consisting mostly of transition-metal oxides, are colored and are sometimes very small in surface area. To overcome this defect, it is desirable to represent the acid–base properties of a catalyst by using another scale, for example, the catalytic activity scale. Many attempts have been made to establish a correlation between catalytic activity and acidity, as have been reviewed in a recent publication (*11*). It has also been reported that the catalytic activities for the dehydration of isopropyl alcohol (IPA) and for the isomerization of *n*-butene, measured in the presence of an excess of air in a continuous-flow system, can be tied to the acidity of the oxidation catalysts (*1–4*). As regards basic catalysts, only a little work has been done on the correlation between catalytic activity and basicity (*12, 13*). Recently, the following ratio has been proposed as an index of the

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basicity of oxidation catalysts (*1–4, 14, 15*):

$$\text{Basicity} \propto \frac{(\text{dehydrogenation activity for IPA})}{(\text{dehydration activity for IPA})}.$$

However, this scale for basicity is not effective when the catalyst is fairly basic and the acidity is low, because the dehydration activity becomes negligibly small compared with the dehydrogenation. In seeking an adequate model of a vapor-phase contact reaction for which the catalytic activity can be well tied to the basicity, we have focused our attention on the decomposition of formic acid.

The decomposition of formic acid proceeds in two directions: dehydration to form CO and dehydrogenation to CO_2. Because of the simplicity of the reaction system, the decomposition provides a good model for fundamental studies of heterogeneous catalysts. Much information has been collected by Mars *et al.* (*16, 17*). Since then, several reports concerning reaction mechanisms have also appeared (*18–21*).

When the catalyst is a metal oxide, it is generally considered that the dehydration reaction is catalyzed by the acidic sites, by analogy with the mechanism established for the catalytic effect of liquid acid (*16, 17*).

As regards the dehydrogenation, Mars *et al.* (*16, 17*) have pointed out that formic acid donates a proton to the catalyst:

$$HCOOH + O\text{–}M \rightarrow HCOO^- + H\text{–}O\text{–}M.$$

The formate intermediate has been supported by ir studies (20). In view of these and Eucken's results (22), it may be proposed that dehydrogenation is catalyzed by the basic sites.

Little attention has been devoted to a direct examination of whether the catalytic activity for the decomposition of formic acid can really be tied to the acid–base properties of the catalyst. Since formic acid is a remarkable reducing agent, the oxide catalysts may be reduced during the reaction, and, as a result, their catalytic activity should be greatly modified. Especially in the cases of oxidation catalysts consisting of oxides of transition metals, it seems impossible to obtain the catalytic activity of a metal oxide the valence states of which are at a steady state. This may be the reason why there is such a large disparity and so much uncertainty in the results reported previously concerning the oxides of transition metals.

It seems possible to obtain the catalytic activity of a metal oxide the valence states of which are at a steady state, if the experiments are performed in the presence of an excess of air and using a continuous-flow reaction system.

In the present work, first, we tried to see how the catalytic activity for the dehydration and the dehydrogenation (oxidative dehydrogenation) were correlated with the acidity and the basicity, respectively, and especially whether the activity for the oxidative dehydrogenation was effective as an index of the basicity. Then, the catalytic activities for both dehydration and dehydrogenation were measured systematically, using various kinds of single and mixed metal oxide catalysts, and the relationship between the catalytic behavior and the acid–base properties was investigated.

EXPERIMENTAL METHODS

Catalysts

Several series of mixed metal oxide catalysts were used in this study. They were prepared as follows. An aqueous solution or slurry containing the required quantities of each metallic component was mixed with 10- to 20-mesh pumice, consisting of 500 ml (about 150 g)/g-atom of metals. The mixture was then evaporated to dryness with vigorous stirring. The catalyst was calcined in a stream of air at 500°C for 4–5 hr. As the starting materials, we used nitrates for Bi, Ni, Zn, and Fe; ammonium salts of oxy acid for V, Mo, and W; acetate for U; chlorides (converted to hydroxides by dilute ammonia) for Ti and Sn; hydrate for K; and H_3PO_4 for P. The pumice used was a natural one originating from volcanic rock in Kagoshima (a southwestern prefecture in Japan), which consists of macropores (the density is about 0.7 g/ml, and the surface area is less than 0.3 m^2/g) and is chemically inert. It was used in our studies merely in order to enhance the mechanical strength of the catalysts.

Basicity Measurements

The basicity of the catalysts was measured by the following three methods.

Static method. CO_2 was chosen as the adsorbate, and the adsorption measurements were carried out using a BET apparatus. About a 20-g portion of the catalyst was put in an adsorption vessel (about 25 ml) and was heat treated at 500°C for 2 hr in a stream of air. Then, the vessel was quickly connected to the adsorption apparatus and was pumped until the catalyst had been cooled to room temperature. A known amount of CO_2 was introduced into the adsorption vessel, and it was allowed to stand for 20 min before the pressure changes were read. Care was taken to adjust the amount of CO_2 in such a way that the final pressure was around 300 mm Hg. Subsequently, the catalyst was pumped for 30 min at the same temperature. Similar adsorption procedures were then repeated, and the amount of readsorption was measured. The amount of CO_2 irreversibly adsorbed at the pressure of 300 mm Hg was obtained as the difference between the amount of readsorption and that of the first adsorption; it was adopted as a measure of the basicity.

Gas-chromatographic pulse technique. Acetic acid was chosen as the adsorbate. The apparatus used was a conventional gas chromatograph (column = PEG 20 *M*, 4 m, 100°C) equipped with a U-tube of stainless steel (40 cm in length and 4 mm i.d.). The catalyst (1.0 g) was packed in the U-tube and was heat treated at 500°C for 2 hr in a stream of air. Immediately after the U-tube had been taken out of the furnace, it was quickly connected to the gas chromatographic column and was placed in another furnace kept at 130°C. Then, the carrier gas (He: 50 ml of NTP/min) was introduced into the system. A sequence of the pulses of an *n*-heptane solution of 1.0 *M* acetic acid was injected into the U-tube at intervals of about 2 min. The volume of a pulse was 5–50 μl, which was adjusted to be about one-tenth of the total amount of adsorption obtained by preliminary measurements. The acetic acid uptake was obtained from the gas-chromatographic analysis at both the inlet and outlet of the U-tube. The peak of acetic acid at the outlet is not observed upon the initial injections, while, as the number of pulse increases, the catalyst is saturated with acetic acid, and so the peak appears. Thus, the amount adsorbed can be evaluated. Subsequently, the carrier gas was allowed to pass through for 30 min at the same temperature. Then the same procedures were repeated, and the amount readsorbed was obtained. The amount irreversibly adsorbed was obtained as the difference between the amount of readsorption and that of the first adsorption; it was adopted as a measure of the basicity.

Titration method. The catalyst (1.0 g) was ground and calcined in air at 500°C for 3 hr and then was put in *n*-heptane (about 30 ml). The sample was titrated with an *n*-heptane solution of 0.02 *N* benzoic acid, using bromthymol blue ($pK_a = 7.1$) and phenolphthalein ($pK_a = 9.3$) as indicators (*12*, *13*).

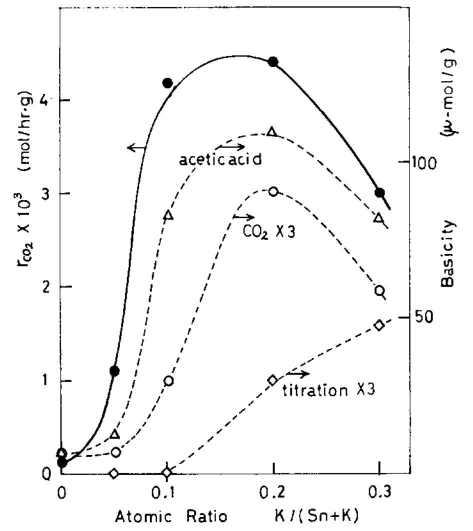

FIG. 1. Relation between the catalytic activity for oxidative dehydrogenation of formic acid to CO_2 and the basicity of SnO_2–K_2O: (●) activity (r_{CO_2}) at 209°C; (○) CO_2 at 20°C (static method); (△) acetic acid at 130°C (pulse method); (◇) titration.

Reaction Procedures

The vapor-phase decomposition of formic acid was carried out in an ordinary continuous-flow reaction 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 well controlled. The concentration of formic acid was 1.2 mol% in air, and the total flow rate was kept constant at 1.5 liters/min (at 25°C). The particle size of the catalyst was 10–20 mesh, and the amount of catalyst weighed 1–20 g. The effluent gas from the reactor was led successively into four chilled water scrubbers to recover the unreacted formic acid. At the end of 1 hr, the contents of the scrubbers were collected (about 300 ml) and analyzed by titration with 0.1 *N* sodium hydroxide. The other compounds were analyzed by means of gas chromatography. The reactor and other experimental procedures were the same as those employed previously (*1–4, 14, 15*).

RESULTS

Correlation between Basicity and Catalytic Activity

The relationship between the basicity and the activity for the decomposition of formic acid was investigated for several series of binary oxide catalysts the basicity of which could be easily measured by different methods. These were the SnO_2–K_2O, ZnO–K_2O, Bi_2O_3–K_2O, Bi_2O_3–MoO_3, and Bi_2O_3–P_2O_5 systems. The main products were CO_2 and H_2O. The amount of CO was negligibly small, and no H_2 was detected. Therefore, it can be said that only the oxidative dehydrogenation takes place over these catalysts which are rather basic. The surface areas of these catalysts were of the order of 1–3 m^2/g, as determined by the BET method using nitrogen at −196°C (see Table 1), and the dependence of these values upon the catalyst composition was not important.

SnO_2–K_2O system. The basicity of SnO_2–K_2O with different K/Sn ratios, as determined by the three different methods, are shown together with the activity for the

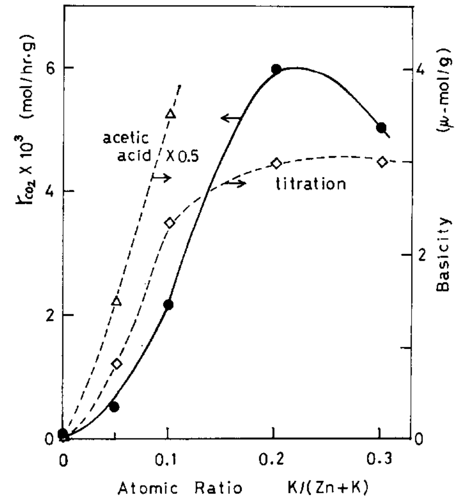

FIG. 2. Relation between the catalytic activity for oxidative dehydrogenation of formic acid to CO_2 and the basicity of ZnO–K_2O: (●) activity (r_{CO_2}) at 214°C; (△) acetic acid at 130°C (pulse method); (◇) titration.

decomposition of formic acid to CO_2 in Fig. 1. A parallelism is found between the values of basicity obtained by the adsorption of CO_2 and that of acetic acid, though the absolute values are fairly different. The basicity, as could reasonably be expected, increases with an increase in the K_2O content in the $K < 0.2$ atom% range. A relatively good correlation is obtained between the values of basicity and catalytic activity.

ZnO–K_2O system. The basicity and the catalytic activity of ZnO–K_2O are plotted in Fig. 2. The amounts of CO_2 adsorbed on the ZnO–K_2O system were too small to obtain reliable data. A rough parallelism is found between the values of basicity obtained by the two different methods. A correlation is observed between the basicity and the activity.

Bi_2O_3–K_2O system. The pure Bi_2O_3 catalyst did not change the color of such indicators as bromthymol blue and phenolphthalein, though it adsorbed a fairly large amount of such acidic molecules as CO_2 and acetic acid. Therefore, the titration method is not suitable to measure the basicity of Bi_2O_3-based catalysts.

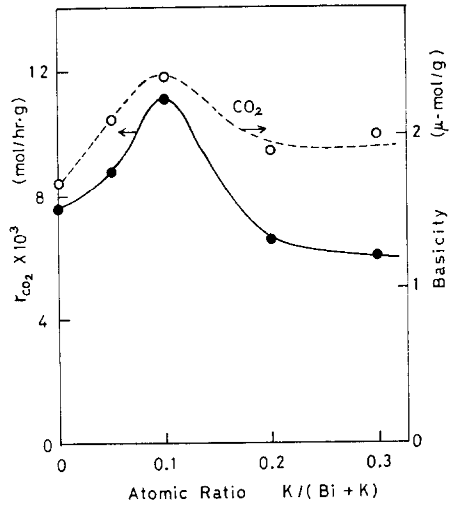

FIG. 3. Relation between the activity for oxidative dehydrogenation of formic acid to CO_2 and the basicity of Bi_2O_3–K_2O: (●) activity (r_{CO_2}) at 155°C; (○) adsorption of CO_2 at 20°C.

The basicity and catalytic activity are plotted in Fig. 3. A correlation can be observed between the basicity obtained by adsorption of CO_2 and the catalytic activity.

Bi_2O_3–MoO_3 and Bi_2O_3–P_2O_5 systems. The basicity of the catalysts is shown in Fig. 4, together with the catalytic activity. As can

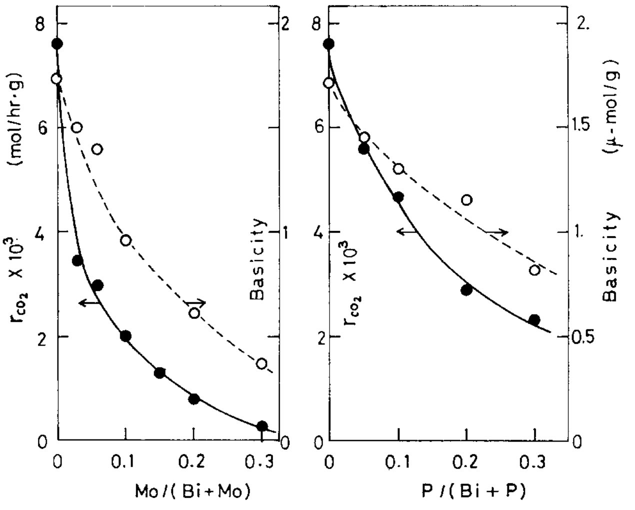

FIG. 4. Relation between the activity for oxidative dehydrogenation of formic acid to CO_2 and the basicity of Bi_2O_3–MoO_3 and Bi_2O_3–P_2O_5: (●) activity (r_{CO_2}) at 155°C; (○) adsorption of CO_2.

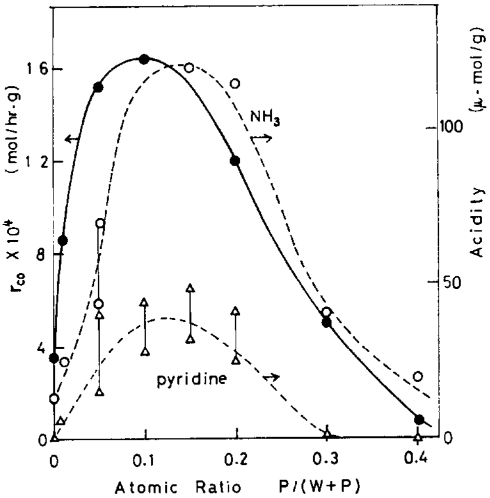

FIG. 5. Relation between the catalytic activity for dehydration of formic acid to CO and the acidity of WO_3–P_2O_5: (●) activity (r_{CO}) at 190°C; (○) NH_3 at 200–250°C (static method); (△) pyridine required to poison the isomerization activity for 1-butene at 160°C (pulse method).

reasonably be expected, the basicity decreases with an increase in the contents of the acidic elements. Correlations are also observed between basicity and catalytic activity.

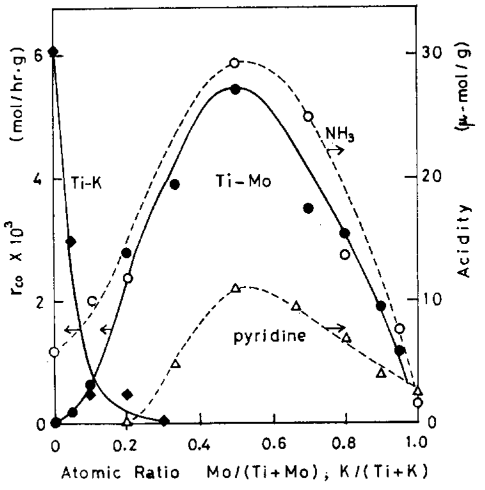

FIG. 6. Relation between the activity for dehydration of formic acid to CO (r_{CO}) and the acidity of catalysts: (●) activity of TiO_2–MoO_3 at 200°C; (◆) activity of TiO_2–K_2O at 270°C; acidity of TiO_2–MoO_3 (○) adsorption of NH_3 at 250°C (static method); (△) pyridine required to poison the isomerization activity for 1-butene.

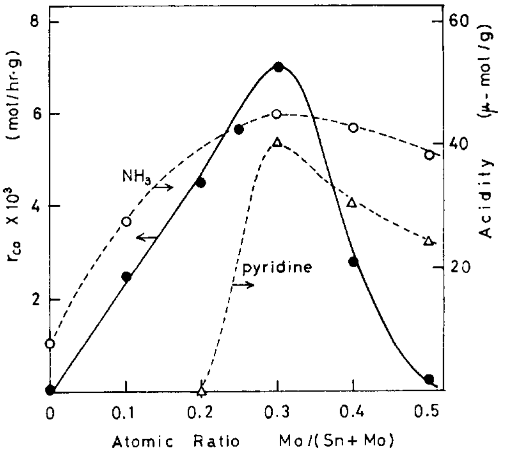

FIG. 7. Relation between the activity for dehydration of formic acid to CO and the acidity of SnO_2–MoO_3: (●) activity (r_{CO}) at 187°C; (○) adsorption of NH_3 at 250°C; (△) pyridine required to poison the isomerization activity for 1-butene.

Correlation between Acidity and Catalytic Activity

The relationship between acidity and catalytic activity was examined. The reaction was carried out using several series of binary oxide catalysts the acidities of which had been obtained previously. In the case of the catalysts, which are acidic rather than basic, the main products were CO and H_2O, and the amount of CO_2 was very small.

WO_3–P_2O_5 system. Together with the acidity of the WO_3–P_2O_5 system determined in a previous work (*23*), the catalytic activity for the dehydration of formic acid to CO is plotted as a function of the P_2O_5 content in Fig. 5. A good correlation is obtained between the acidity and the catalytic activity.

TiO_2–MoO_3 and TiO_2–K_2O systems. The acidity of the TiO_2–MoO_3 system (*3*) and the dehydration activity for formic acid are plotted in Fig. 6. The results show a

TABLE 1

Catalytic Activity and Selectivity of Metal Oxides for Decomposition of Formic Acid[a]

Catalyst	Atomic ratio	Area (m^2/g)	Amount used (g)	Temperature (°C)	Conversion (%) to	
					CO	CO_2
V		2.7	10	237	46	(5)[b]
V–Mo	(6/1)	3.4	10	237	54	(4)[b]
V–Ti	(5/5)	2.6	6	237	62	(5)[b]
W		8.2	20	200	40	0
W–K	(9/1)	7.4	20	230	50	3
W–Mo	(9/1)	9.2	20	190	48	0
W–P	(9/1)	3.4	20	175	58	0
Mo–P	(8/2)	0.6	20	302	27	0
Mo–Ti	(5/5)	13.3	20	214	50	0
Mo–Sn	(3/7)	22	20	165	60	0
U		5.5	12	296	54	—[c]
U–K	(9/1)	5.2	12	296	4	—[c]
U–Mo	(9/1)	4.1	12	296	28	—[c]
U–P	(9/1)	4.6	12	296	33	—[c]
Ti		2.0	10	220	45	0
Ti–K	(9/1)	3.1	20	255	12	—
Ti–Mo	(9/1)	6.4	10	220	40	0
Ti–P	(9/1)	11.3	10	190	52	0
Sn		3.3	20	236	25	35
Sn–K	(9/1)	3.1	20	183	2	33
Sn–Mo	(9/1)	11.7	20	190	60	0
Sn–P	(9/1)	3.1	20	236	56	2
Fe		10.7	20	260	8	55
Fe–K	(9/1)	8.1	20	230	0	50
Fe–Mo	(9/1)	19	20	192	50	2
Fe–P	(9/1)	41	20	240	50	8
Bi		1.0	2	155	0	33
Bi–K	(9/1)	1.2	2	155	0	50
Bi–Mo	(9/1)	1.6	2	155	0	9
Bi–P	(9/1)	1.7	2	155	0	23
Zn		1.0	20	260	0	65
Zn–K	(9/1)	1.1	20	190	0	25
Zn–P	(9/1)	1.1	20	260	0	25
Ni		10.3	13	240	0	50
Ni–K	(9/1)	13.7	17	200	0	62
Ni–P	(9/1)	12	19	260	1	35

[a] Formic acid = 1.2 mol% in air; total flow rate = 1.5 liters/min.

[b] Approximate value.

[c] Near zero.

correlation between the acidity and the dehydration activity.

The dehydration activity of the TiO_2–K_2O system is also plotted in Fig. 6. With an increase in the K_2O content, which may reasonably decrease the acidity of the catalysts, the dehydration activity decreases.

SnO_2–MoO_3 system. The acidity of the SnO_2–MoO_3 system (*2*) and the dehydration activity are plotted in Fig. 7. A correlation is observed between the acidity and the dehydration activity.

Catalytic Activity of Various Metal Oxides for the Decomposition of Formic Acid

Another series of experiments was carried out using various kinds of single and mixed metal oxide catalysts. The results obtained at the formic acid conversion of about 50% are listed according to the sequence of the acid–base properties of the metal oxides obtained previously on the basis of the catalytic activities for the dehydration and dehydrogenation of IPA (*14*).

The results in Table 1 may be summarized as follows.

(i) Formic acid is decomposed exclusively by dehydration to CO when the catalyst is based on an oxide which is more acidic than SnO_2 (see Table 1).

(ii) Formic acid is decomposed exclusively by oxidative dehydrogenation to CO_2 and H_2O when the catalyst is based on an oxide which is more basic than Fe_2O_3 (see Table 1).

(iii) Both dehydration and oxidative dehydrogenation occur with the catalysts based on SnO_2 and Fe_2O_3, the acid–base properties of which are intermediate between those two groups of oxides mentioned above. The SnO_2-based catalysts are more favorable for the dehydration and less favorable for the oxidative dehydrogenation than are the Fe_2O_3-based catalysts.

(iv) When an acidic element such as MoO_3 and P_2O_5 is added to an acidic oxide (i.e., oxides of W, Mo, U, Ti, Sn, or Fe), the dehydration activity always increases. This may be attributed to the increase in the acidity. The MoO_3–SnO_2, WO_3–P_2O_5, and TiO_2–P_2O_5 catalysts, which have very high acidities (*2, 23, 24*), are very active for the dehydration.

(v) When a basic element such as K_2O is added to the acidic oxides, the dehydration activity always decreases. However, the addition of a small amount of K_2O to an oxide which is more acidic than SnO_2 (see Table 1) cannot generate the activity for the oxidative dehydrogenation.

(vi) The selectivity as well as the activity of SnO_2 and Fe_2O_3 are greatly modified by the nature of the additives. For example, SnO_2–K_2O and Fe_2O_3–K_2O are oxidative dehydrogenation catalysts, while SnO_2–MoO_3, SnO_2–P_2O_5, Fe_2O_3–MoO_3, and Fe_2O_3–P_2O_5 are dehydration catalysts.

(vii) The addition of K_2O to a basic oxide such as NiO, ZnO, or Bi_2O_3 always increases the oxidative dehydrogenation activity.

(viii) The addition of MoO_3 or P_2O_5 to a basic oxide such as NiO, ZnO, or Bi_2O_3 always decreases the oxidative dehydrogenation activity. However, it cannot generate the dehydration activity.

(ix) Bi_2O_3 shows a surprisingly high oxidative dehydrogenation activity.

DISCUSSION

These experiments demonstrate in a direct way the following regularities.

(I) With rather basic metal oxides, formic acid is decomposed by oxidative dehydrogenation to CO_2 and H_2O, and the activity is correlated with the basicity.

(II) With rather acidic oxides, formic acid is decomposed by dehydration to CO and H_2O, and the activity is correlated with the acidity.

Since the oxidative dehydrogenation of formic acid is a sort of oxidation, the question of whether the reaction is affected by the oxidizing power of the catalysts and the activity cannot be tied merely to the basicity.

We would like to propose the following hypothesis, as discussed in earlier reports (*4, 23, 25*). When a catalyst is potent in oxidizing power, the oxidation reaction can take place without requiring any activation of the reactant molecule. The activity, therefore, is controlled mainly by the ability of catalyst to activate oxygen. This is the case in deep or intense oxidation with oxides of Mn, Co, Cu, and Cr. On the other hand, when the oxidizing power is not so strong, the reaction requires the activation of the reactant molecule; therefore, the catalytic activity is largely governed by the possibility of the reactant activation. This is the case in mild oxidation (*26–29*).

On this basis, it is considered that, so far as the metal oxides which have been dealt with in this study are concerned, the oxidative dehydrogenation of formic acid is dependent preferentially on the activation of formic acid. The basic sites of catalyst, because of their electron-donating ability, serve to adsorb and activate the acidic reactant, such as formic acid. (*1–4, 25*). Actually, the Bi_2O_3-based oxides are dramatically active in the oxidative dehydrogenation of formic acid, while they are very inactive in the oxidation of basic (electron donor type) compounds such as olefinic hydrocarbons (*1, 14*).

The activation of formic acid may be made by a proton transfer from formic acid to a basic site, a lattice oxygen, O^{2-} (*12, 13, 30, 31*) of the catalyst, resulting in the formation of an anionic intermediate, i.e., a formate ion, which may then be stabilized on a metal cation adjacent to the O^{2-}. This view is in conformity with those advanced by earlier investigators (*16–20*). As regards the dehydration of formic acid, another type of activation may be made on the acidic sites of the catalyst, probably by electron transfer from formic acid to the acidic sites, i.e., by the abstraction of H^- from formic acid or by the addition of a surface proton to formic acid, as has been proposed previously (*16–20*).

The clear regularity in the catalytic behavior of metal oxides, obtained from the results shown in Table 1, supports the validity of the sequence of acid–base properties of metal oxides obtained earlier by the catalytic activity scale using the dehydration and dehydrogenation of IPA (*14*).

Indeed, the catalytic activity for the dehydration of formic acid can be measured practically only with oxides which are more acidic than Fe_2O_3 (see Table 1), while the catalytic activity for the oxidative dehydrogenation can be measured only with oxides which are more basic than SnO_2 (see Table 1). This means that the reactions may not take place when the base or acid strength of the catalysts is not sufficient.

In summary, we can say that, as an index of the basicity of solid catalysts, the catalytic activity for the oxidative dehydrogenation of formic acid is effective for basic catalysts, while the (dehydrogenation activity for IPA)/(dehydration activity for IPA) ratio is valid for acidic catalysts.

As an index of the acidity of catalysts, the activity for the dehydration of formic acid is useless in the cases of basic catalysts. Therefore, it can be said that the dehydration of IPA or the isomerization of *n*-butene is better as a model reaction for this purpose.

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