JOURNAL OF CATALYSIS 54, 426–435 (1978)

Catalytic Activity for the Oxidation of Methanol and the Acid–Base Properties of Metal Oxides

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Received January 3, 1978; revised May 17, 1978

The vapor-phase oxidation of methanol was carried out in the presence of an excess of air over many series of composite oxide catalysts, the acidity and basicity of which had been previously determined, such as MoO_3–TiO_2, MoO_3–Fe_2O_3, MoO_3–SnO_2, MoO_3–P_2O_5, MoO_3–Bi_2O_3–P_2O_5, V_2O_5–MoO_3, WO_3- and U_3O_8-based oxides, SnO_2–K_2O, Co_3O_4–K_2O, and Bi_2O_3–X_nO_m (X = P, Mo, W, V, and S), and the relationship between the catalytic behavior and the acid–base properties of the metal oxides was investigated. Formaldehyde can be obtained only from such acidic oxides as MoO_3, WO_3, V_2O_5, and U_3O_8, but not from oxides which are more basic than TiO_2, e.g., TiO_2, Fe_2O_3, SnO_2, Bi_2O_3, ZnO, and Co_3O_4. A clear correlation always exists between the activity for formaldehyde formation and the acidity in the cases of the MoO_3- or V_2O_5-containing catalysts, and the amounts of the by-products are small, except in the case of the MoO_3–SnO_2. Methanol is dehydrated preferentially to ether over the WO_3–P_2O_5 (P/W = 2/98–20/80) catalysts, and no correlation exists between the activity for formaldehyde formation and the acidity. Over the basic oxides, methanol is oxidized mainly to CO_2, and the activity for CO_2 formation is correlated with the basicity of the catalysts. It is concluded that the activation of methanol by acidic sites is a necessary condition for the formation of formaldehyde, that the possibility of this methanol activation mainly decides the oxidation activity, and that the combination of metal oxides contributes to the enhancement or modification of the acidic property.

INTRODUCTION

Formaldehyde is manufactured by the partial air oxidation of methanol, mostly over the MoO_3–Fe_2O_3-based catalysts. This catalytic reaction has been the subject of a number of important investigations (*1–11*); the catalytic behavior has also been investigated in relation to other MoO_3- and V_2O_5-based composite oxides (*12–15*).

What are the functions required for a catalyst in the selective oxidation of methanol? Why can good performance be obtained by the combination of several oxides? The kinetics and the natures of active sites have been studied actively, and the oxidizing agent has been found to be the lattice oxygen (*3, 4*). Trifiro *et al.* (*5, 6*) postulated that the ability for the selective oxidation is connected with the double-bond character of MoO_3, while Jirů *et al.* (*7*) and Pernicone *et al.* (*8*) proposed the participation of acidic sites in the oxidation reaction. Furthermore, Pernicone *et al.* (*9*) considered that the presence of Fe^{3+} ions increases the concentration of methanol-adsorption centers, consisting of an anion vacancy (acidic site) and an O^{2-} ion (basic site). Then, Nováková *et al.* (*10*) concluded that the selective oxidation is caused by Mo^{6+} ions, and that

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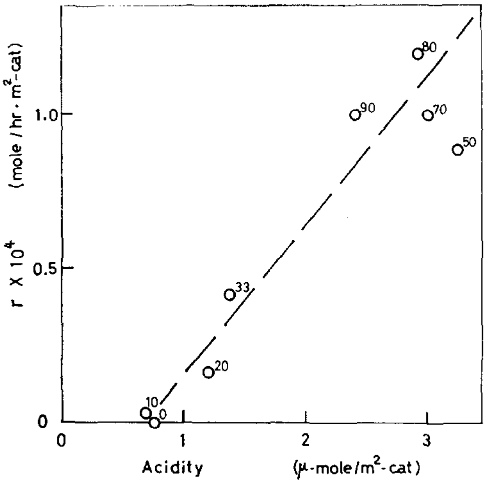


FIG. 1. Catalytic activities for oxidation of methanol to formaldehyde and acidities of MoO_3–TiO_2 oxides: activity (r) at 255°C, $CH_3OH = 2.5\%$ in air; acidity = amount of NH_3 irreversibly adsorbed at 200°C. Numbers correspond to the content (atomic percent) of molybdenum in the MoO_3–TiO_2.

Fe^{3+} ions hinder the reduction of the Mo^{6+} ions and increase the lability of the lattice oxygen available for the oxidation process. Recently, Sala and Trifirò (*11*) stated that Fe_2O_3 is able to adsorb and activate the gaseous oxygen and that the role of Fe^{3+} is to make easier the reoxidation of the molybdenum ions reduced by the organic molecule.

On the other hand, we have recently proposed that an acid–base-type interaction between the catalyst surface and the organic substance to be oxidized plays the determining role in selective oxidation and that the combination of metal oxides contributes to a modification of the acid–base properties (*16–25*). According to the views proposed by the above-cited investigators (*7–11*), it can be predicted that there is something in common between the catalytic behavior in the oxidation of methanol and the acid–base properties of the catalyst.

The purpose of the present study is to demonstrate, in a direct manner, how the activity and selectivity correlate with the acid–base properties with regard to various types of composite oxide catalysts and to extract from the results a principle useful for the understanding of the catalytic function of metal oxides.

EXPERIMENTAL METHODS

The catalysts used in this study were various MoO_3-, V_2O_5-, WO_3-, and Bi_2O_3-based composite oxides, SnO_2–K_2O, and Co_3O_4–K_2O, with different compositions, and several U_3O_8-, ZnO-, and NiO-based oxides. They were the same as those used in previous works, and so their acidity and basicity, numbers of acidic and basic sites had already been determined (*17–24*).

The vapor-phase oxidation of methanol was carried out in an ordinary continuous-flow reaction system. The reactor was a steel tube coated with aluminum, 50 cm in length and 1.8 cm in internal diameter. It was mounted vertically and immersed in a lead bath, the temperature of which was well controlled. Liquid methanol was

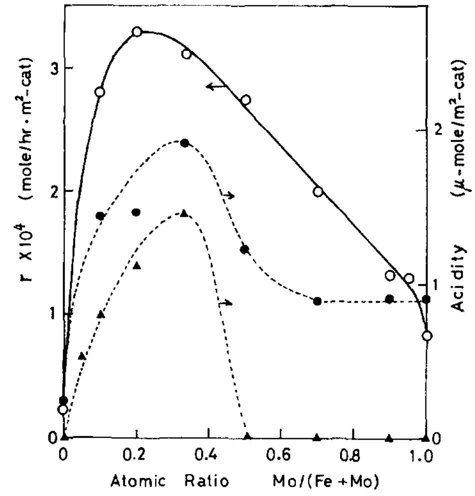


FIG. 2. Catalytic activities for oxidation of methanol to formaldehyde and acidities of MoO_3–Fe_2O_3 oxides: (○) activity (r) at 257°C, $CH_3OH = 2.5\%$ in air; acidity = (●) amount of NH_3 irreversibly adsorbed at 200°C (static method), (▲) amount of pyridine required to poison the isomerization activity for 1-butene at 130°C (pulse method),

TABLE 1

Oxidation of Methanol with Mo/Sn = 30/70 Catalyst[a]

Reaction temperature (°C)	Total conversion[b] (%)	Yield (mole%) of HCHO	HCOOH	$HCOOCH_3$	CO	CO_2
187	23	11.5	1.3	8	0	0
198	57	18.0	5.3	17	0	0
207	76	27	11	23	1.7	1.8
226	90	32	9.5	17	19	3.5
252	97	19.6	4.5	1.5	76	6.1

[a] Amount of catalyst used = 5.0 g; CH_3OH = 2.5 mole% in air; total flow rate = 1.0 liter/min.

[b] Obtained from the consumption of methanol.

introduced into a preheating section of the reactor by means of an infusion syringe pump; the concentration of the methanol was 2.5 mole% in air. The total flow rate was kept constant at 1.0 liters/min (at 25°C), while the amount of catalyst was varied in the range of 2 to 20 g. The effluent gas from the reactor was led successively into four chilled water-scrubbers to recover the water-soluble compounds. At the end of 1 hr, the contents of the scrubbers were collected (about 300 ml). The formaldehyde was analyzed by means of iodometry (*27*), the formic acid, by titration with 0.1 *N* NaOH, and the other compounds, by means of gas chromatography. The other experimental procedures were the same as those employed in the previous works (*17–26*).

RESULTS

A. MoO_3–TiO_2 Catalysts

The oxidation was carried out at 195 to 280°C over a series of MoO_3–TiO_2 catalysts, with different compositions, which were the same as those used in a previous study (*17*). The main product was formaldehyde, and the yield of CO_2 was less than 1 to 2 mole%, even at a conversion of above 50%. The amounts of the other products were negligibly small. For example, with 10 g of the Mo/Ti = 33/67 (atomic ratio) catalyst, the yields of formaldehyde were 1.1, 3.0, 8.1, 18.2, and 35.7 mole% at 195, 220, 237, 255, and 277°C, respectively.

The initial rate of the formaldehyde formation at 255°C, *r* (mole/hr m^2-catalyst), was measured for each catalyst as an index of the catalyst activity. Following the principle of the differential reactor, the conversion was held at a low level, i.e., usually below 25%. The amount of the catalyst was controlled to achieve a proper conversion. The rates are shown in Fig. 1, as a function of the acidity (number of acidic sites) of the catalysts (*17*). A correlation is observed between the activity and the acidity.

B. MoO_3–Fe_2O_3 Catalysts

The MoO_3–Fe_2O_3 catalysts, especially the Mo/Fe = 5/95 to 50/50 catalysts, were more active than the MoO_3–TiO_2 catalysts, and the formation of by-products was small. For example, when 5 g of the Mo/Fe = 20/80 catalyst was used, the yield of formaldehyde was 53 mole% at 257°C. The initial rates of the formaldehyde formation at 257°C are plotted in Fig. 2, together with the acidities of the catalysts obtained previously (*18*). The activity varies in the same direction as the acidity.

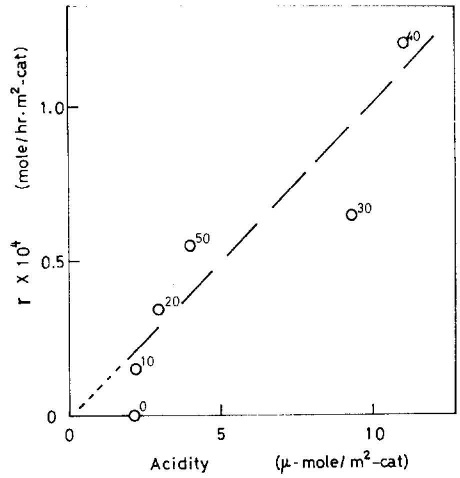


FIG. 3. Catalytic activities for oxidation of methanol to formaldehyde and acidities of MoO_3–SnO_2 oxides: activity (r) at 198°C, $CH_3OH = 2.5\%$ in air; acidity = amount of NH_3 irreversibly adsorbed at 200°C. Numbers correspond to the content (atomic percent) of molybdenum in the MoO_3–SnO_2.

C. *MoO_3–SnO_2 Catalysts*

The MoO_3–SnO_2 catalysts, especially those with Mo/Sn = 10/90 to 50/50, were considerably more active for the methanol oxidation than the MoO_3–TiO_2 and MoO_3–Fe_2O_3 catalysts. For example, even at 200°C, about 60% of the methanol was consumed with 5 g of the Mo/Sn = 30/70 catalyst. However, the selectivity to formaldehyde was low, about 30 to 50 mole%. Significant amounts of formic acid and methyl formate were produced. At a higher temperature (250°C), the main product was CO. Some representative results are shown in Table 1. The initial rate of the formaldehyde formation at 198°C was chosen as an index of the oxidation activity; it is plotted in Fig. 3, as a function of the acidity of the catalysts. An interrelationship is also obtained in this case.

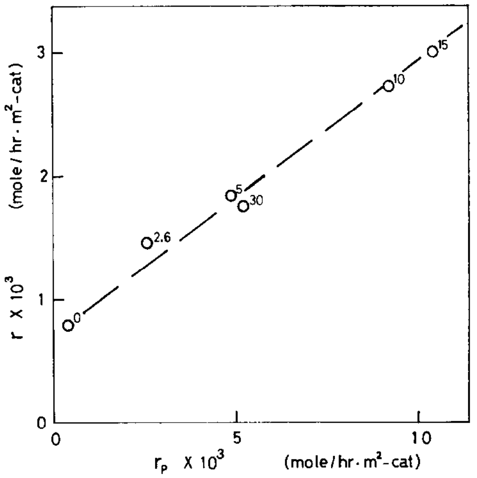


FIG. 4. Catalytic activities for oxidation of methanol to formaldehyde and acidities of MoO_3–P_2O_5 oxides: activity (r) at 350°C, $CH_3OH = 2.5\%$ in air; acidity = dehydration activity for IPA (r_p) at 185°C, IPA = 1.65% in air. Numbers correspond to the content (atomic percent) of phosphorus in the MoO_3–P_2O_5.

D. *MoO_3–P_2O_5 Catalysts*

The MoO_3–P_2O_5 catalysts were much less active than the MoO_3–TiO_2, –Fe_2O_3, and –SnO_2 catalysts, and so a relatively high temperature was required to achieve a proper conversion. For example, with 10 g of the P/Mo = 10/90 catalyst the yields of formaldehyde were 7.2, 18.0, 34, and 55 mole% at 257, 300, 330, and 365°C,

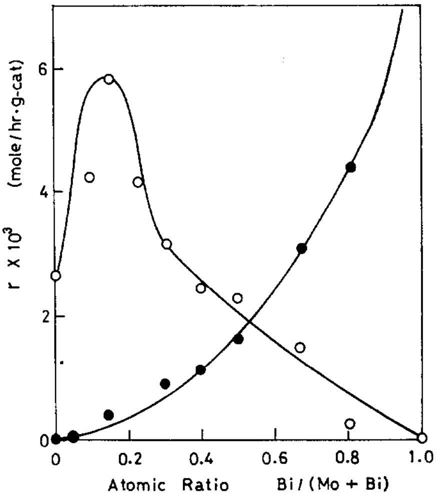


FIG. 5. Oxidation activities of MoO_3–Bi_2O_3–P_2O_5 (P/Mo = 0.2) catalysts: (○) activity for oxidation of methanol to formaldehyde, (●) activity for CO_2 formation at 350°C, $CH_3OH = 2.5\%$ in air.

respectively. The main product was formaldehyde, while the other compounds were formed in negligibly small quantities. The initial rates of the formaldehyde formation at 350°C are plotted in Fig. 4, as a function of the dehydration activity for isopropyl alcohol (IPA), which is used as a measure of the acidity of the catalysts (*19*). A good correlation is observed between the two activities.

E. *MoO_3–Bi_2O_3–P_2O_5 Catalysts*

When the content of Bi_2O_3 was low (Bi/Mo < 0.2), formaldehyde was almost the sole product; however, the formation of CO_2 increased with an increase in the Bi_2O_3 content (Fig. 5). The rates of formaldehyde formation at 350°C are shown as a function of the acidity of the catalysts (*20*) in Fig. 6. The rates of CO_2 formation at 350°C are also shown as a function of the basicity (*20*) in Fig. 7. The results indicate that the activity for formaldehyde formation is correlated with the acidity, while the activity for CO_2 formation is correlated with the basicity.

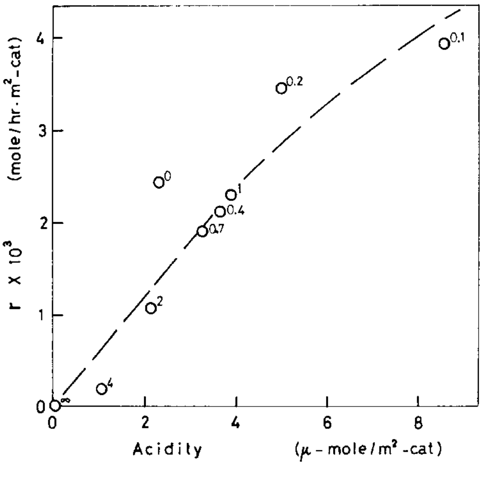


FIG. 6. Relation between the activity for oxidation of methanol to formaldehyde and the acidity of the MoO_3–Bi_2O_3–P_2O_5 (P/Mo = 0.2) catalysts: activity (r) at 350°C, CH_3OH = 2.5% in air; acidity = amount of NH_3 irreversibly adsorbed at 200°C. Numbers in the figure are the Bi/(Mo + Bi) ratios.

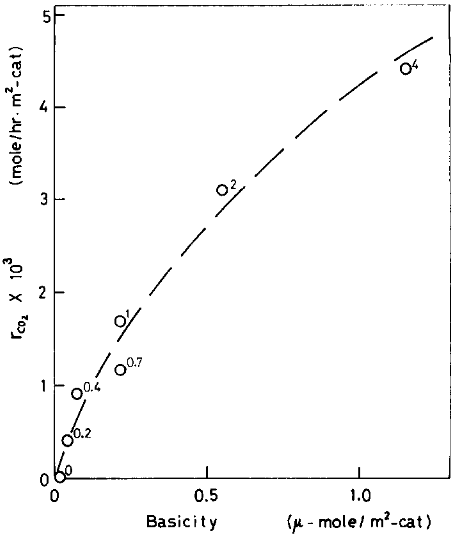


FIG. 7. Relation between the activity for oxidation of methanol to CO_2 and the basicity of the MoO_3–Bi_2O_3–P_2O_5 (P/Mo = 0.2) catalysts: activity (r_{CO_2}) at 350°C; basicity = amount of CO_2 irreversibly adsorbed at 25°C. Numbers in the figure are the Bi/(Mo + Bi) ratios.

F. *V_2O_5–MoO_3 Catalysts*

The V_2O_5–MoO_3 system was chosen as an example of V_2O_5-based catalysts. The

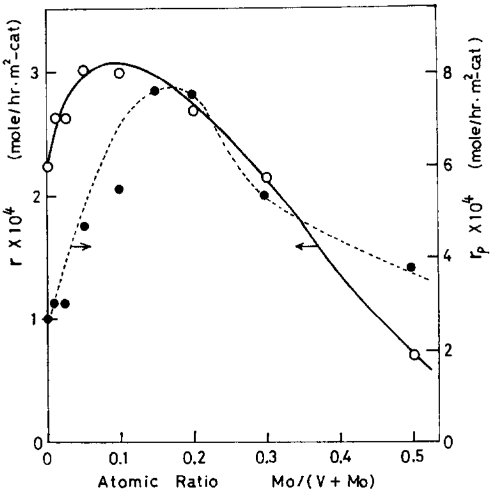


FIG. 8. Catalytic activities for oxidation of methanol to formaldehyde and acidities of V_2O_5–MoO_3 oxides: (○) activity (r) at 230°C, CH_3OH = 2.5% in air; (●) acidity = dehydration activity for IPA at 180°C, IPA = 1.65% in air.

V_2O_5–MoO_3 catalysts were as active as the MoO_3–SnO_2 catalysts, and their main product was also formaldehyde. The rates of formaldehyde formation at 230°C are shown in Fig. 8, together with the dehydration activity for IPA, which is adopted as a measure of the acidity (*21*). The two activities vary in approximately the same direction.

G. *WO_3–P_2O_5 and Other WO_3-Based Catalysts*

The WO_3–P_2O_5 catalysts, especially those with P/W = 5/95 to 20/80, were extremely active for methanol consumption, even at 200°C. However, the product was mainly dimethyl ether, and the yield of formaldehyde was 6 to 7 mole% at a total conversion of 70 to 80%. The other oxidation products were formed in negligibly small quantities, even at 280°C. The rates of formaldehyde formation at 277°C are shown in Fig. 9, as a function of the acidity (*22*). The activity is not correlated with the acidity.

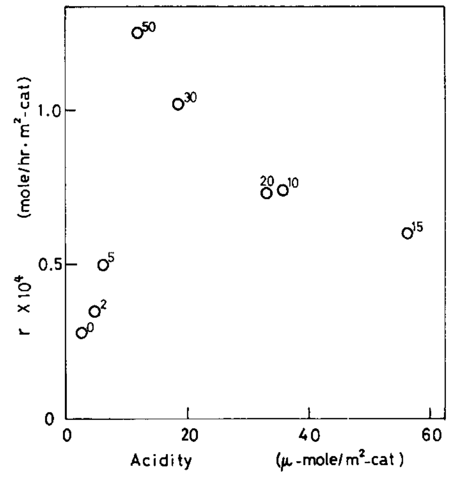


FIG. 9. Catalytic activities for oxidation of methanol to formaldehyde and acidities of WO_3–P_2O_5 oxides: activity (r) at 277°C; acidity = amount of NH_3 irreversibly adsorbed at 200°C. Numbers correspond to the content (atomic percent) of phosphorus in the WO_3–P_2O_5.

TABLE 2

Oxidation of Methanol with WO_3-Based Catalysts[a]

Catalyst Atomic ratio	Area (m^2/g)	Yield to HCHO (mole%)
W	8.2	4.7
W–Mo 9–1	9.2	44.
W–P 9–1	8.0	4.0
W–V 8–2	8.	87.
W–K 9–1	7.4	3.6

[a] Temperature = 320°C; amount of catalyst used = 10. g; CH_3OH = 2.5 mole% in air; total flow rate = 1.0 liter/min.

Some representative results obtained from several WO_3-based catalysts are shown in Table 2. Formaldehyde was almost the sole oxidation product in the case of these catalysts as well.

H. *U_3O_8-Based Catalysts*

Pure U_3O_8 was also effective for the formaldehyde formation, and the formation of by-products was not important, though the activity was lower than that of pure V_2O_5. The results are shown in Table 3.

I. *SnO_2–K_2O Catalysts*

Pure SnO_2 is scarcely active at all for formaldehyde formation, but it gives CO_2 at higher temperatures. The rates of CO_2 formation from methanol were measured for the SnO_2–K_2O catalysts at 285°C. They are plotted in Fig. 10, as a function of the

TABLE 3

Oxidation of Methanol with U_3O_8-Based Catalysts[a]

Catalyst Atomic ratio	Area (m^2/g)	Yield to HCHO (mole%)
U	5.5	41.2
U–Mo 9–1	4.1	20.1
U–P 9–1	4.6	35.4
U–K 9–1	5.2	8.2

[a] Temperature = 300°C; amount of catalyst used = 10. g; CH_3OH = 2.5 mole% in air; total flow rate = 1.0 liter/min.

basicity of the catalysts (*23*). The activity increases with an increase in the basicity.

J. *Co_3O_4–K_2O Catalysts*

The Co_3O_4-based catalysts were very active for the oxidation to CO_2. The rates of CO_2 formation at 180°C are shown in Fig. 11, as a function of the basicity (*24*). A clear correlation is obtained between the activity and the basicity.

K. *Bi_2O_3-Based Catalysts*

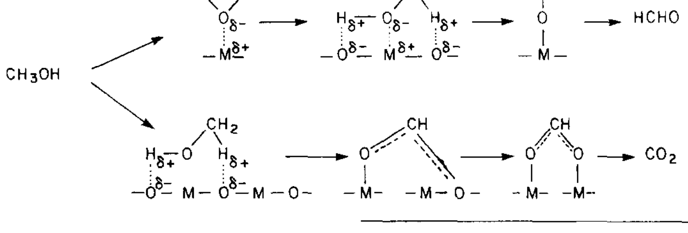
Pure Bi_2O_3 also has no function for the formaldehyde formation and gives mainly CO_2. A correlation has previously been obtained (*25*) between the activity for the CO_2 formation and the basicity, regardless of any change in the kind and amount of the second component added to Bi_2O_3. The results are shown in Fig. 12.

DISCUSSION

As regards the acid–base properties of the transition-metal oxides, the following sequence (number of sites and site strength are given together) has previously been proposed on the basis of the catalytic activities for the dehydration and dehydrogenation of IPA (*16, 26*) and for the decomposition of formic acid (*23*); $V_2O_5 > WO_3 > MoO_3 > U_3O_8 > TiO_2 > SnO_2 > Fe_2O_3 > Bi_2O_3 > ZnO > NiO$, Co_3O_4, $CuO > MgO > K_2O$. Methanol is oxidized to formaldehyde over an acidic oxide such as V_2O_5, MoO_3, WO_3, or U_3O_8, and CO_2 is obtained when the catalyst is a relatively basic oxide such as TiO_2 SnO_2, Fe_2O_3, Bi_2O_3, ZnO, NiO, or Co_3O_4. It is evident as a general rule that formaldehyde can be obtained only by using acidic metal oxides.

This principle is also valid in the cases of composite oxides. Formaldehyde is the main product so long as the catalyst is acidic enough, and the selectivity to formaldehyde decreases and that to CO_2 increases with an increase in the basic property (Fig. 5).

Since methanol is a molecule containing an oxgen atom which has a high electronegativity, it has two different characters, electron-donating and electron-accepting: $C^{\delta+}$–$O^{\delta-}$–$H^{\delta+}$. Therefore, methanol is susceptible to attack by either acidic or basic sites of metal oxides. When methanol is attacked and activated by acidic sites of metal oxides, it is oxidized to formaldehyde. On the other hand, when methanol is attacked and activated by basic sites of oxides, it is oxidized to CO_2. It is therefore believed that the difference in the manner of methanol activation brings about the difference in the products. According to Pernicone *et al.* (*9*) and Nováková *et al.* (*10*), formaldehyde is formed via an alcoholate bound to an acidic site. On the other hand, according to Miyata *et al.* (*28*), CO_2 is formed via a formate. Thus, the following reaction scheme may be supposed:



As has already been mentioned, the presence of an acidic property is a necessary condition for a catalyst effective in regarding formaldehyde formation. However, this condition alone is not always sufficient. Since the formation of formaldehyde is an

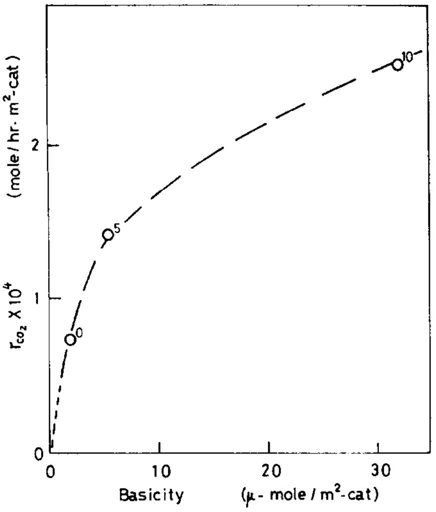


FIG. 10. Relation between the catalytic activity for oxidation of methanol to CO_2 and the basicity of the SnO_2–K_2O oxides: activity (r_{CO_2}) at 285°C, CH_3OH = 2.5% in air; basicity = amount of CO_2 irreversibly adsorbed at 25°C. Numbers correspond to the content (atomic percent) of potassium.

oxidation reaction, the oxidizing function, i.e., the intrinsic oxidation activity (*16, 18, 20, 24*), is required for a catalyst as well as the ability to activate the methanol molecule, though the activity is not necessarily determined by this oxidizing function. In the cases of the WO_3–P_2O_5 catalysts with P/W = 5/95 to 20/80, for example, methanol is mainly dehydrated to ether rather than oxidized to formaldehyde and the activity for formaldehyde formation is not correlated with the acidity. These results can be explained by the characteristics of the acid-base properties; that is, by the fact that the WO_3–P_2O_5 catalysts are strikingly acidic, but scarcely basic and, accordingly, are lacking in the oxidizing function (*22*). Thus, in the case of this catalyst system, the oxidation activity is controlled by the oxidizing function rather than by the activation of methanol on acidic sites. This finding is in line with the results obtained in the oxidation of olefins with the WO_3–P_2O_5 system (*22*). On the other hand, it can also be said that the dehydration of methanol to ether is possible only with acidic oxides which are lacking in the oxidizing function or in the basic property.

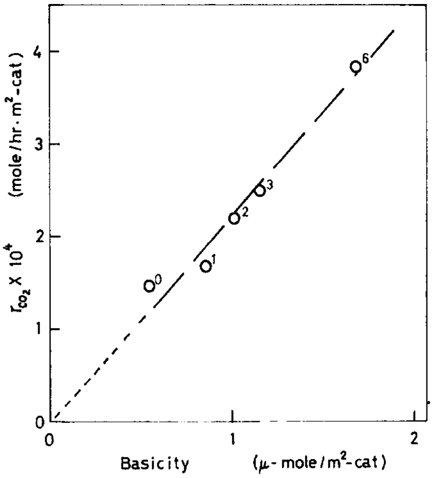


FIG. 11. Relation between the catalytic activity for oxidation of methanol to CO_2 and the basicity of the Co_3O_4–K_2O oxides: activity (r_{CO_2}) at 180°C, CH_3OH = 2.5% in air; basicity = amount of CO_2 irreversibly adsorbed at 25°C. Numbers correspond to the content (atomic percent) of potassium.

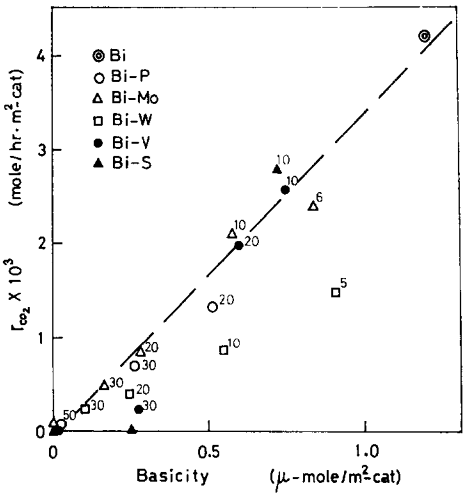


FIG. 12. Catalytic activities for oxidation of methanol to CO_2 and basicities of Bi_2O_3-based binary oxides: activity (r_{CO_2}) at 300°C, CH_3OH = 2.5% in air; basicity = amount of CO_2 irreversibly adsorbed at 25°C, numbers correspond to the content (atomic percent) of the second components.

In the cases of the MoO_3- and V_2O_5-based oxides, a correlation always exists between the catalytic activity for formaldehyde formation and the acidity (number of acidic sites) of the catalysts, so long as the additive is the same compound. This finding indicates that the activity for formaldehyde formation is largely governed by the activation of methanol on acidic sites rather than by the oxidizing function. When the additive is different, however, it is hard to correlate the activity with the acidity. The results agree with those obtained previously in the cases of the oxidation of olefins (*16–21*) and lead us to consider similarly that the nature of the acidic sites, e.g., the acid strength, may vary depending on the nature of the additive.

On this basis, it can be postulated that the combination of foreign oxides with an acidic oxide, such as MoO_3 and V_2O_5, contributes to the enhancement or modification of the acidic properties. Though the effect of the combination of metal oxides on the oxidizing function is still open to doubt, this function seems not to play a determining role in the selective oxidation.

As regards the acidic property, another condition also seems to be required for an effective catalyst. For instance, the MoO_3–SnO_2 catalyst with Sn/Mo = 70/30 is highly acidic and, as a result, very active in the oxidation of methanol as well as in the oxidation of olefins, but it catalyzes the side reactions, i.e., the formation of formic acid and methyl formate, too. It is considered that, when the acidic property of a catalyst is too high, the formaldehyde produced, which is an electron-donating (basic) compound, is activated by the acidic sites and, then, oxidized to formic acid. The formic acid is further esterified also by the aid of the acidic sites. The fact that formic acid is decomposed to CO with acidic catalysts (*23*) suggests that CO, which is the main product in the oxidation of methanol on the MoO_3–SnO_2 under severe conditions, is formed via formic acid. Therefore, it can be stated that a moderate character for the acid is required in order to avoid the consecutive oxidation of the produced formaldehyde. This may be the reason why the MoO_3–SnO_2 catalysts, which are much more active in the oxidation of methanol than the MoO_3–Fe_2O_3 catalysts, cannot be used as practical catalysts.

It may be concluded that the activity and selectivity in the oxidation of methanol can be understood in terms of the acid–base properties of the catalysts. We would like to propose here also that the combination of metal oxides contributes to the enhancement or modification of the acidic properties.

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