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The Oxidation Activity and Acid-Base Properties of Co_3O_4-V_2O_5 and Co_3O_4-MoO_3 Systems

Mamoru Ai

Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

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The acidity and basicity of Co_3O_4–V_2O_5 and Co_3O_4–MoO_3 systems, with different compositions, were measured by means of the adsorption of NH_3, pyridine, and CO_2. The values of acidity were also confirmed by studying the catalytic activity for acid-catalyzed reactions, such as the dehydration of isopropyl alcohol and the isomerization of 1-butene. With the addition of V_2O_5 or MoO_3, the basicity rapidly decreases and the acidity gradually increases. The catalytic activity for the oxidation of hexane is well correlated with the basicity of the catalysts. With the Co_3O_4-rich catalysts, $V/(Co+V)$ or $Mo/(Co+Mo)<0.4$, butadiene is mainly oxidized to CO_2; the rate is also correlated to the basicity. However, the Co_3O_4-poor catalysts, $V/(Co+V)$ and $Mo/(Co+Mo)>0.6$, show a good selectivity for the maleic anhydride formation. The Co_3O_4-containing catalysts, regardless of the composition, are not effective for the selective oxidation of butene to butadiene. In the oxidation of methanol, the Co_3O_4-rich catalysts give only CO_2. However, with the Co_3O_4-poor catalysts, formaldehyde is almost the sole product. It is concluded that the catalytic behavior is to be interpreted, to a considerable extent, in terms of the acid-base properties of the metal oxides.

Co_3O_4 is a typical metal oxide with an eminent oxidizing power; it is, therefore, employed as a main component of catalysts suitable for the complete combustion of organic compounds. In the preceding paper,[1] we reported on the Co_3O_4-based catalysts modified by controlling the amount of P_2O_5 and K_2O added. It was found that the catalytic activity for the complete oxidation of various types of reactants, such as hexane, butene, phenol, and methanol, was correlated with the basicity of the catalysts.

It is interesting to note that, as a component of mixed-oxide catalysts suitable for certain selective oxidations, Co_3O_4 is also employed.[2] What is the role of Co_3O_4 in the multi-component catalysts?

In this work, Co_3O_4 was combined with an acidic oxide, such as V_2O_5 and MoO_3, which are widely used as the main components of various catalysts suitable for selective oxidation. We attempted to find how the addition of V_2O_5 or MoO_3 to Co_3O_4 modifies the catalytic behavior and to see whether or not the oxidation activity and selectivity for different types of oxidations can be interpreted in terms of the acid-base properties of the composite oxides.

Experimental

The catalysts used in this study were two series of binary oxides, Co_3O_4–V_2O_5 and Co_3O_4–MoO_3, with different compositions. As the starting materials, $Co(NO_3)_2 \cdot 6H_2O$, NH_4VO_3, and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were used. They were prepared by the procedures described in the preceding paper.[1]

The acidity and the basicity of the catalysts were determined by studying the adsorption of basic and acidic molecules, such as NH_3, pyridine, and CO_2, from the gas phase using either the static or pulse method. The technique of the measurements has also been described previously.[1,3–6]

The vapor-phase oxidation of 1-butene, butadiene, hexane, and methanol, the isomerization of 1-butene, and the dehydration of isopropyl alcohol (IPA) were carried out in an ordinary continuous-flow reaction system. The reactor and the experimental procedures were the same as those employed in earlier works.[1,3–7]

Results

Surface Areas. The effect of the V_2O_5 and MoO_3 content on the specific surface area was first checked by the BET method using nitrogen at −196 °C. The results are shown in Table 1. The surface area increases gradually with the addition of V_2O_5 or MoO_3 and reaches a broad maximum when the amount of the second components is about 10 at %.

Table 1. Surface areas of the Co_3O_4–V_2O_5 and Co_3O_4–MoO_3 catalysts used

Composition $V/(Co+V)$	Surface area (m^2/g)	Composition $Mo/(Co+Mo)$	Surface area (m^2/g)
0	4.0	0	4.0
0.01	4.9	0.01	6.3
0.02	5.7	0.02	7.2
0.04	6.3	0.04	8.8
0.07	7.3	0.06	8.7
0.10	9.6	0.08	8.2
0.15	8.3	0.10	10.7
0.20	8.0	0.15	8.8
0.30	7.6	0.20	8.6
0.50	6.6	0.30	8.3
0.70	3.8	0.40	6.3
0.80	4.7	0.50	4.7
0.90	3.7	0.60	3.6
1.00	3.2	0.70	4.0
		0.80	3.2

Acidity. Since pure Co_3O_4 has a fair amount of acidic sites, probably of a weak acid strength compared with those of V_2O_5 and MoO_3, NH_3 was adsorbed on the Co_3O_4-rich catalysts to the same extent as on the V_2O_5- and MoO_3-rich catalysts, even at 175 °C. At higher temperatures, the decomposition of NH_3 was enhanced because of the eminent oxidizing power of Co_3O_4. Therefore, it seems difficult to measure the acidity by means of the NH_3 adsorption.

Therefore, another attempt was made to determine the acidity; that is, the amount of pyridine required to poison the isomerization activity for 1-butene was measured by the pulse method in the same way as in earlier studies.[3–5,7] A difficulty arose in this method, too, especially in the case of the Co_3O_4-rich catalysts, because they exhibit a very low isomerization activity; moreover, they oxidize the adsorbed pyridine at high temperatures. The results are shown in Figs. 1 and 2.

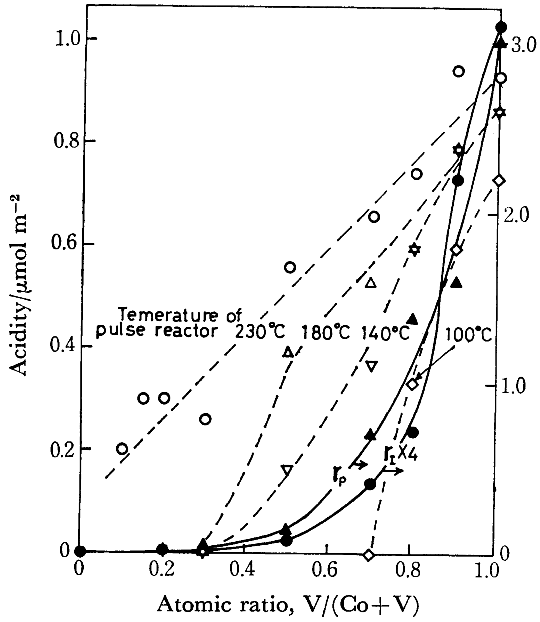

Fig. 1. Acidity of Co_3O_4–V_2O_5 as a function of the V_2O_5 content. Amount of pyridine required to poison the isomerization of 1-butene (pulse method): broken line, dehydration activity for IPA at 187 °C (r_p): ▲, isomerization activity for 1-butene at 260 °C (r_I): ●.

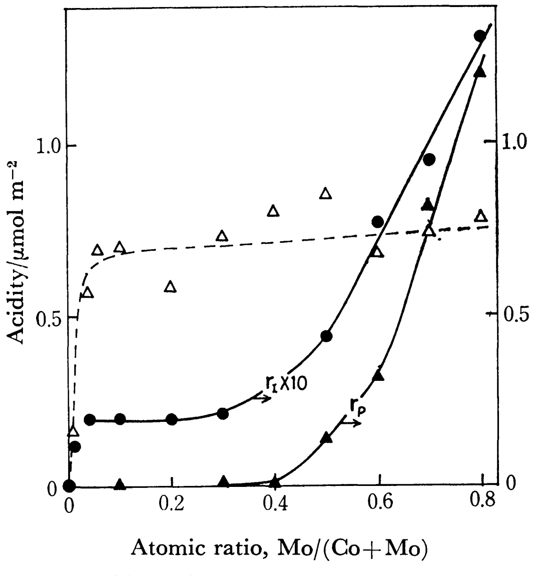

Fig. 2. Acidity of Co_3O_4–MoO_3 as a function of the MoO_3 content. Amount of pyridine required to poison the isomerization of 1-butene at 175 °C (pulse method): △, broken line, dehydration activity for IPA at 187 °C (r_p): ▲, isomerization activity for 1-butene at 272 °C (r_I): ●.

In order to confirm the values of the acidity, the catalytic activity for certain 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.[3–5,7] The reactions were carried out at the IPA and butene concentrations of 1.33 and 1.0 mol % in air, and at the total flow rate of 1.0 l/min, by changing the amount of catalyst in the range from 1 to 20 g. The initial rate of IPA dehydration at 187 °C, r_p, and that of butene isomerization at 260 or 272 °C, r_I (mol h^{-1} m^{-2} of catalyst), are plotted together with the values of acidity, in Figs. 1 and 2.

Basicity. The basicity of the Co_3O_4-containing catalysts, as determined by the amounts of CO_2 irreversibly adsorbed at 20 °C, is plotted in Fig. 3.

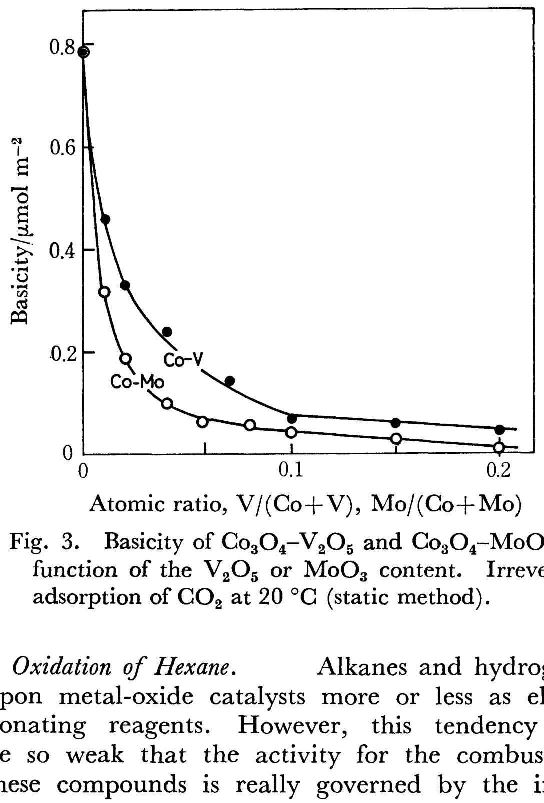

Fig. 3. Basicity of Co_3O_4–V_2O_5 and Co_3O_4–MoO_3 as a function of the V_2O_5 or MoO_3 content. Irreversible adsorption of CO_2 at 20 °C (static method).

Oxidation of Hexane. Alkanes and hydrogen 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 rather than by the activation of the reactant molecules.[1,3,8] For convenience in the experimental procedures, combustion of hexane was chosen as a model reaction which reflects the intrinsic oxidation activity of the catalysts.

The reaction was carried out keeping the following conditions constant at T=262 °C; hexane=0.6 mol % in air, and total flow rate=1.0 l/min, while the amounts of the catalysts were varied in the range from 1 to 20 g to achieve a proper conversion. The main product was CO_2. The initial rate of CO_2 formation, r_{CO_2}(mol h^{-1} m^{-2} of catalyst), was measured with each catalyst as an index of the activity. The results are plotted as a function of the basicity of the catalysts in Fig. 4. A fairly good correlation is obtained between the activity and the basicity.

Oxidation of Butadiene. As a model reaction of "acid-formation" reactions, the oxidation of butadiene

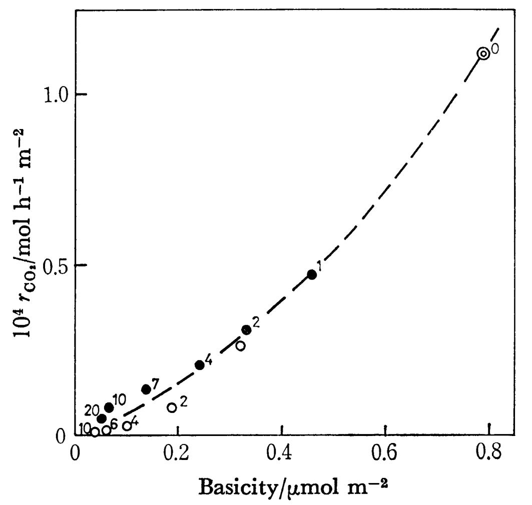

Fig. 4. Relation between the basicity and the oxidation activity for hexane. Co_3O_4–V_2O_5: ●, Co_3O_4–MoO_3: ○. r_{CO_2}: rate of CO_2 formation at $T = 262$ °C and hexane $= 0.6$ mol % in air. Numbers correspond to the content (atomic percent) of V_2O_5 or MoO_3 in the binary oxides.

to maleic anhydride was chosen in the same way as in the previous studies.[3–5,7)] The reaction was carried out in the temperature range from 250 to 480 °C, at the butadiene concentration of 1.0 mol % in air, and with a total flow rate of 1.0 l/min, by changing the amounts of the catalysts from 1 to 20 g. The Co_3O_4-rich catalysts, V/(Co+V) and Mo/(Co+Mo)<0.4, were very active. However, the main product was CO_2, and the amount of CO were far lower than those of CO_2. The maleic anhydride, acetic acid, and the other compounds were formed in negligibly small amounts. The initial rates of CO_2 formation at 255 °C for the Co_3O_4–V_2O_5 and at 275 °C for the Co_3O_4–MoO_3, r_{CO_2}(mol/h·m^2 of catalyst), are plotted as a function of the basicity of the catalysts in Fig. 5.

On the other hand, the Co_3O_4-poor catalysts, V(Co+V) and Mo/(Co+Mo)>0.6, were fairly inactive compared with the Co_3O_4-rich catalysts. However, they were selective in forming acidic products. The selectivity to maleic anhydride at a fixed conversion, 50 to 60%, is shown in Fig. 6.

Oxidation of 1-Butene. As a model of the "base-formation" reactions, the oxidation of butene to

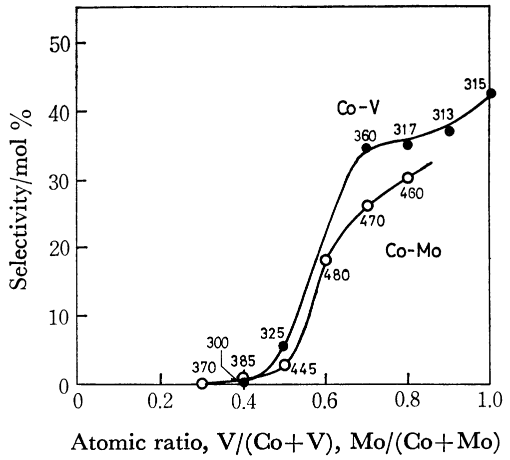

Fig. 6. Selectivity of butadiene to maleic anhydride as a function of the catalyst composition. Co_3O_4–V_2O_5: ●, Co_3O_4–MoO_3: ○. Conversion=50—60%, butadiene=1.0 mol % in air. Numbers correspond to the reaction temperatures (°C).

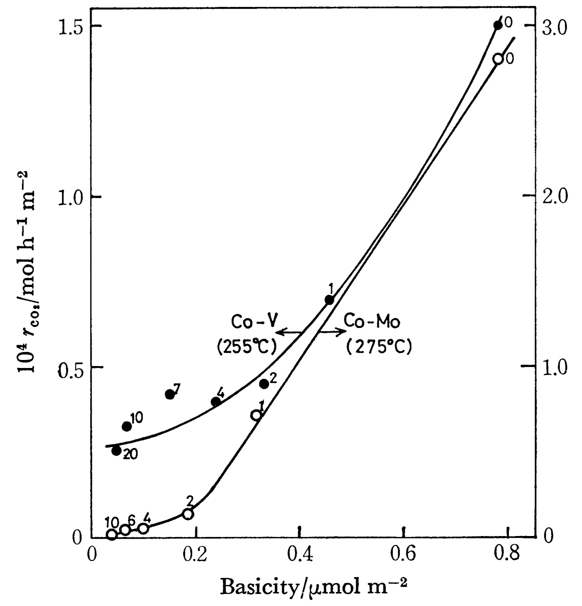

Fig. 5. Relation between the basicity and the activity for the oxidation of butadiene to CO_2. Co_3O_4–V_2O_5 (255 °C): ●, Co_3O_4–MoO_3 (275 °C): ○. Butadiene $= 1.0$ mol% in air. Numbers correspond to the content (atomic percent) of V_2O_5 or MoO_3.

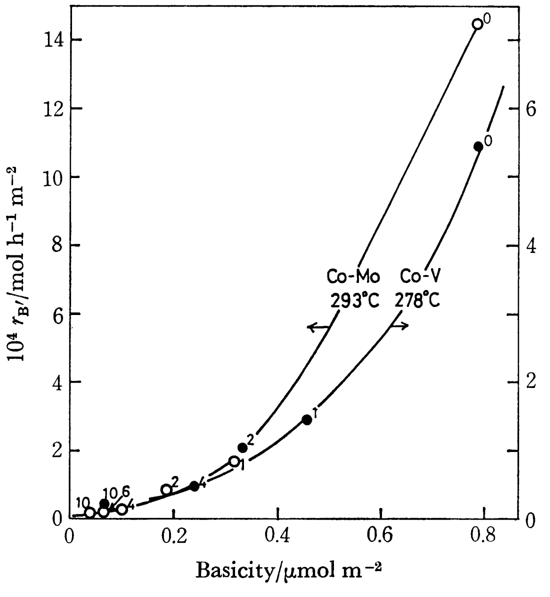

Fig. 7. Relation between the basicity and the activity for the oxidation of 1-butene to butadiene. Co_3O_4–V_2O_5 (278 °C): ●, Co_3O_4–MoO_3 (298 °C): ○. Concentration: 1-butene–oxygen–nitrogen=1.0–1.0–98.0 mol %. Numbers correspond to the content (atomic percent) of V_2O_5 or MoO_3.

butadiene was investigated.[3–5,7] The reaction was carried out in the temperature range from 270 to 420 °C, keeping the conditions constant at the concentrations of 1-butene, oxygen, and nitrogen of 1.0, 1.0, and 98.0 mol % respectively, and at the total flow rate of 1.0 l/min, while the amounts of the catalysts were varied in the range from 1 to 20 g. The main products were butadiene, CO_2, and CO; the amounts of the other products were very small.

The initial rates of butadiene formation at 278 °C for the Co_3O_4–V_2O_5 and at 293 °C for the Co_3O_4–MoO_3, r_β' (mol h^{-1} m^{-2} of catalyst) are plotted as a function of the basicity of the catalysts in Fig. 7. The selectivity to butadiene is shown in Fig. 8.

Oxidation of Methanol. Since it has been found that the catalytic activity and selectivity in the oxidation of methanol can be interpreted in terms of the acid-base properties of the catalysts,[9] the catalytic behavior of the Co_3O_4-containing catalysts for methanol oxidation was investigated.

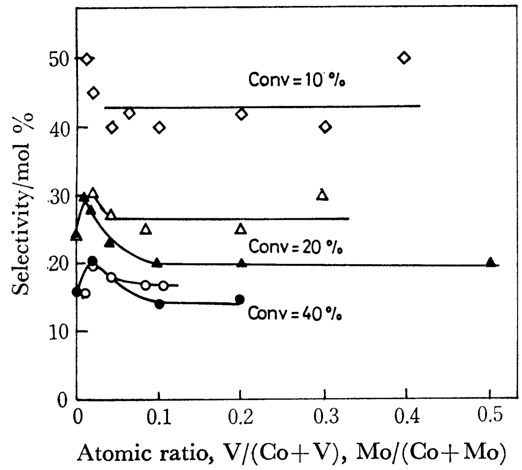

Fig. 8. Selectivity of 1-butene to butadiene as a function of the catalyst composition. Co_3O_4–V_2O_5: ▲ ●, Co_3O_4–MoO_3: ◇ △ ○. T=270—420 °C.

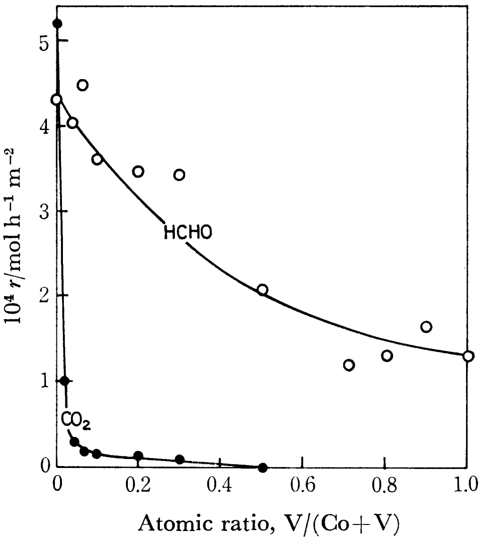

Fig. 9. Activity of Co_3O_4–V_2O_5 for the oxidation of methanol. Formaldehyde: ○, CO_2: ●. T=193 °C, methanol=2.6 mol % in air.

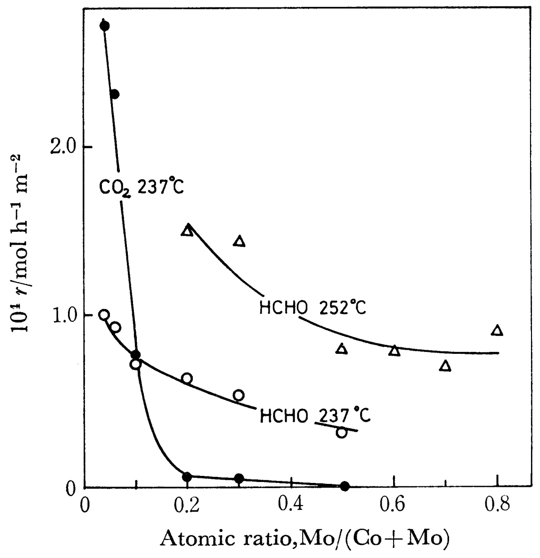

Fig. 10. Activity of Co_3O_4–MoO_3 for the oxidation of methanol. Formaldehyde: ○ △, CO_2: ●. Methanol =2.6 mol % in air.

The reaction was carried out at 193 °C for the Co_3O_4–V_2O_5 and at 237 and 252 °C for the Co_3O_4–MoO_3. The methanol concentration was 2.6 mol % in air, the total flow rate was 1.0 l/min, and the amounts of the catalysts used were from 1 to 20 g. The main products were formaldehyde and CO_2, and the amounts of the other products were very small. The initial rates of formaldehyde and CO_2 formation, r_F and r_{CO_2}(mol h^{-1} m^{-2} of catalyst), were measured following the principle of the differential reactor. The results are shown in Figs. 9 and 10.

Discussion

In the case of the Co_3O_4–V_2O_5 catalysts, the catalytic activities for the two acid-catalyzed reactions varied in the same direction as do the values of acidity (Fig. 1). We would like here to advance the theory that the amounts of pyridine required to poison the isomerization at different temperatures reflect the numbers of acidic sites with different acid-strengths; that is, the activity at a low temperature corresponds to the number of acidic sites of a strong acid-strength. According to the theory, it may be supposed from Fig. 1 that the V_2O_5 or V_2O_5-rich catalysts have stronger acidic sites than do the Co_3O_4-rich catalysts.

In the case of the Co_3O_4–MoO_3 system, however, a large discrepancy in the shape of curves is observed between the acidity and the activities for the acid-catalyzed reactions. Taking into consideration the fact that, because of the low isomerization activity, reliable data cannot be obtained even by the pulse method, especially in the Co_3O_4-rich catalysts, it is believed that the catalytic activities reflect the true acidity better than the amounts of pyridine. That is, the acidity of the Co_3O_4–MoO_3 increases steadily with an increase in the MoO_3, as in the case of the Co_3O_4–V_2O_5 system.

From the results shown in Figs. 1—3 and the above consideration, the following arguments may be put forward. The generation of marked acidic or basic properties is not observed upon the combination of Co_3O_4 with V_2O_5 or MoO_3. As can easily be expected from the acidic nature of V_2O_5 and MoO_3, the basicity of Co_3O_4 is extinguished rapidly with a small amount of these additives. In contrast, the acidity increases steadily with the content of the acidic oxides; in other words, the acidity of the acidic oxides is rapidly extinguished by combination with a basic oxide such as Co_3O_4.

The results shown in Fig. 4 indicate that the activity for hexane oxidation is independent of the acidity of the catalyst and is dependent on the basicity. This finding is in line with the results obtained from the Co_3O_4–P_2O_5 and Co_3O_4–K_2O systems.[1]

The results shown in Figs. 5 and 7 indicate that, even for the oxidation of olefins, the activity of the Co_3O_4-rich catalysts is correlated with the basicity rather than with the acidity of the catalysts. With regard to this finding, we would make the following proposal.

As has been proposed in the previous studies,[1,5,7] the oxidation activity is governed generally by three functions; (i) the activation of olefin by acidic sites; (ii) the activation of gaseous oxygen, which is connected with the basic character, and (iii) the oxidizing power of the surface oxygen species. The Co_3O_4-rich catalysts are poor in the acidic property; consequently, their ability to activate olefin is low, and, moreover, they have an extremely high oxidizing power. Possibly, a sufficient activation of the olefin by acidic sites is not a necessary condition for the oxidation and the reaction is mainly decided by the (ii) function and the (iii) function. This is the reason why the oxidation activity for olefin is correlated with the basicity.

On the other hand, the results in Fig. 6 indicate that the Co_3O_4-poor catalysts are effective for the "acid-formation-type" oxidation. This finding is also in line with the results obtained with other V_2O_5- and MoO_3-based catalysts and supports the proposal that a requirement for an effective catalyst for "acid-formation" reaction is the possession of a sufficient acidic property.[1,3–5,7]

With regard to the oxidation of butene to butadiene, both the Co_3O_4–V_2O_5 and Co_3O_4–MoO_3 are not effective over a full range of compositions. To explain the results, the following consideration is envisaged as a possibility. When the contents of V_2O_5 or MoO_3 are low, the oxidizing power is so strong that the reaction without the activation of butene on acidic sites takes place non-selectively. On the other hand, when the content of V_2O_5 or MoO_3 are high, the oxidizing power is highly suppressed; this is surely one of the necessary conditions for any type of selective-oxidation catalyst. However, another condition is also required for an effective catalyst for the "base-formation-type" oxidation; that is, the possession of a moderate character both in the acid and the base is required for the butadiene formation.[1,3–5] The V_2O_5- and MoO_3-rich catalysts are too acidic to be satisfactory for this type of oxidation.

Actually, the Co_3O_4-containing catalysts are proposed as catalysts suited only for "acid-formation" reactions such as the synthesis of acrylic acid[2,10] and of methacrylic acid.[2]

As for the oxidation of methanol, the activity to form CO_2 (Figs. 9 and 10) varies in the same fashion as does the basicity (Fig. 3). This finding supports the view that the CO_2 formation is catalyzed by the basic sites.[9] However, it seems difficult to explain the activity for formaldehyde formation merely by the acidity, as in the previous study.[9] At any event, it is also true in the case of the Co_3O_4-containing catalysts that formaldehyde is the sole product as long as the catalysts are acidic enough and that the selectivity to formaldehyde decreases, and that of CO_2 increases, with an increase in the basic properties.[9]

It can be concluded that the acidic and basic properties of the Co_3O_4-containing mixed oxides are modified, as can be expected from the acidic nature of the additives, and that the catalytic behavior in oxidation is to be interpreted, to a considerable extent, in terms of the acid-base properties.

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