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The Relationship between the Oxidation Activity and the Basicity of Modified Co_3O_4 Catalysts

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In order to clarify the relationship between the intrinsic oxidation activity and the basicity of metal oxide, the vapor-phase oxidation of *n*-hexane, 1-butene, phenol, and methanol was carried out in the presence of an excess of air with two series of Co_3O_4-based catalysts, the acid–base properties of which had been modified by controlling the amounts of either K_2O or P_2O_5. The main product was CO_2, regardless of the reactants used. The catalytic activity for the oxidation of all the reactants was correlated with the basicity of the catalysts, except in the cases were the K_2O content was high (K > 2 atom%). No correlation was observed between the activity and the acidity. With the addition of more than 3 atom% K_2O, the oxidation activity for *n*-hexane and 1-butene sharply decreases, an the catalysts containing 10 atom% K_2O are almost inactive for these reactants. However, the oxidation activity for phenol and methanol remains active even after the addition of 6 to 10 atom% K_2O. It is considered that, in the case of such catalysts, the oxidation activity is no longer governed by the intrinsic oxidation activity, but by the activation of the reactants at the basic sites. The results demonstrate that the intrinsic oxidation activity is associated with the basic property of metal oxide.

INTRODUCTION

Since a contact oxidation is a reaction between an organic compound and the oxygen on the surface of metal oxide, the reaction may be governed by the following four factors or functions: (i) the activation of the reactant molecule; (ii) the reactivity of the reactant molecule; (iii) the activation of oxygen, i.e., the possibility of the incorporation of gaseous oxygen into the crystal-lattice oxygen (O^{2-}) by electron transfer from the metal oxide to the oxygen (*1, 2*), which is connected with the ability to reoxidize the active sites available for the oxidation reaction (*3, 4*); and (iv) the reactivity of oxygen, i.e., the oxidizing power of the surface oxygen species.

The second factor is largely dependent on the nature of the reactant molecule. Thus, the main requirements for an oxidation catalyst are factors i, iii, and iv.

The idea was advanced in earlier studies (*5–7*) that the activation of the reactant molecule is associated with an acid–base-type interaction between the reactant molecule and metal oxide and that this function plays a determining role in the catalytic activity and selectivity of mild oxidation.

Function iii above,

$$\underset{\text{(Lewis base)}}{M^{(n-x)+}} + \underset{\text{(acceptor)}}{(x/4)O_2} \rightarrow M^{n+} + \underset{\text{(Brønsted base)}}{(x/2)O^{2-}}, \tag{1}$$

is dependent on (a) the electron-donating ability, i.e., the base strength, of the metal ion in a lower oxidation state, and (b) the

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number of active lattice-oxygen sites, i.e., the basicity. It may be expressed as:

$$\text{Function iii} \propto (\text{basicity}) \cdot f(\text{base strength}). \quad (2)$$

On the other hand, the function iv is associated with the strength of the metal–oxygen bonding (M–O). The combination of functions iii and iv is defined as the "intrinsic oxidation activity." It may be written as:

$$\text{Intrinsic oxidation activity} \propto (\text{basicity}) \cdot f(\text{M–O and base strength}). \quad (3)$$

Following the lead of Sabatier (*8*) and Balandin (*9*), the relationship between the oxidation activity and the strength of metal–oxygen bonding has been studied by many investigators (*10–15*). A very rough correlation was found in the cases of certain single metal oxides, though there were a number of exceptions. It is clear that an explanation based merely on function iv is insufficient, even in the case of total oxidation.

As regards function iii, the oxidation activity has also been investigated actively in connection with the electrical conductivity, the electron work function, and the relative Fermi energy (*16–19*). Hattori *et al.* (*20*) reported that the oxidation activity of lanthanide oxides for butane is correlated with the fourth ionization potential as a measure of the stability of the teravalent ion relative to the trivalent ion.

In order to interpret more perfectly the catalytic action of metal oxides: (a) it is necessary to take into account the number of active sites as well as the nature; (b) the properties of the surface should be dealt with; (c) the properties to be connected with the catalytic action should be measured directly from the same catalyst; and (d) the properties measured by a chemical process (e.g., the acid–base property) may be preferred to the properties measured by a physical process (i.e., an electrical method).

These considerations led us to confirm the relationship between the basicity properties and the intrinsic oxidation activity of metal oxide. However, how can the intrinsic oxidation activity be evaluated, since, as has been mentioned above, the oxidation activity is governed, more or less, by two functions, that is: (I) the activation of the reactant molecule and (II) the intrinsic oxidation activity? To solve this problem, we would like to propose the following hypothesis, discussed in earlier reports (*6, 7*): When the oxidizing power of a catalyst is weak, the reaction requires a sufficient activation of the reactant molecule. Thus, the oxidation activity is decided predominantly by the activation of the reactant molecule rather than by the intrinsic oxidation activity. On the other hand, when the metal–oxygen bonding strength is weak and the oxidizing power is eminent, the reaction can take place without a sufficient activation of the reactant molecule. Thus, the predominant factor deciding the oxidation activity is the intrinsic oxidation activity rather than the activation of the reactant molecule.

In the present paper, Co_3O_4 was chosen as a model of the metal oxides with eminent oxidizing power; accordingly, their oxidation activity is decided mainly by the intrinsic oxidation activity. The modification of the acid–base properties was achieved by combining different amounts of K_2O or P_2O_5. The catalytic activity for the oxidation of different types of organic compounds, such as paraffinic hydrocarbon, olefin, acidic compound, and alcohol, was examined. Then, the relationship between the intrinsic oxidation activity and the basicity of the catalysts was investigated.

EXPERIMENTAL METHODS

Catalysts. Two series of Co_3O_4-based binary oxide catalysts, Co_3O_4–K_2O and Co_3O_4–P_2O_5, with different compositions were prepared as follows. Aqueous KOH

TABLE 1

Surface Areas of the Co_3O_4–K_2O and Co_3O_4–P_2O_5 Catalysts

Composition K/(Co + K)	Surface area (m^2/g)	Composition P/(Co + P)	Surface area (m^2/g)
0.0	2.4	0.0	2.4
0.01	2.8	0.05	5.1
0.02	2.6	0.10	6.0
0.03	2.1	0.20	5.8
0.06	2.5	0.30	5.5
0.10	2.6		

or H_3PO_4 solutions were added to $Co(NO_3)_2 \cdot 6H_2O$ solutions, and then 10- to 20-mesh pumice (surface area, <0.3 m^2/g) originating from volcanic rocks was mixed into the solutions. The amount of pumice was 500 ml (about 150 g)/g-atom of the metals. The mixtures were then evaporated to dryness with vigorous stirring. The catalysts were calcined in a stream of oxygen at 500°C for 4 to 5 hr. The surface areas were measured by the BET method using nitrogen at −196°C.

Acidity and basicity measurements. Since the Co_3O_4-based oxides are colored, the acidity and basicity were determined by studying the adsorption of basic and acidic molecules, respectively, from the gas phase, using the static method. NH_3 and CO_2 were chosen as the adsorbates. The amount of adsorption at a pressure of 300 mm Hg was measured volumetrically. Subsequently, the catalyst was pumped out for 30 min at the same temperature. Similar adsorption procedures were repeated, and the amount of readsorption was measured. The amount of irreversible adsorption was defined as the difference between the amount of readsorption and that of the first adsorption. This was adopted as the measure of the acidity or basicity. The details of the procedures were the same as those described in previous papers (*6*).

Oxidation procedures. The vapor-phase oxidations of *n*-hexane, 1-butene, phenol, and methanol were 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 concentrations of the *n*-hexane, 1-butene, phenol, and methanol were 0.39, 0.67, 0.54, and 1.7 mole% in air, respectively. The total flow rate was kept constant at 1.5 liters/min, while the amounts of catalysts used were varied in the range from 1 to 20 g. The experimental procedures were the same as those employed in the previous works (*5*, *6*).

RESULTS

Acidity and Basicity

The surface areas of the Co_3O_4–K_2O and Co_3O_4–P_2O_5 are shown in Table 1. The surface area increases upon the addition of P_2O_5, while it remains approximately the same upon the addition of K_2O.

The acidity and basicity per unit of surface area of Co_3O_4–K_2O and Co_3O_4–P_2O_5, as determined by the amount of NH_3 irreversibly adsorbed at 183°C and the amount of CO_2 adsorbed at 25°C, respectively, are plotted as a function of either the K_2O or the P_2O_5 content in Figs. 1 and 2.

Pure Co_3O_4 has both acidic and basic sites, though the characters are not prominent. The acidity decreases and the basicity increases, steadily, with an increase in the K_2O content, as can be easily expected from the nature of K_2O. In the case of the Co_3O_4–P_2O_5 system, the basicity sharply decreases with the P_2O_5 content, but no increase in the acidity was observed upon the addition of P_2O_5 up to 30 atom%.

Correlation between Basicity and Oxidation Activity

The relationship between the basicity of the Co_3O_4-based oxides and their catalytic activity for oxidation in the presence of an

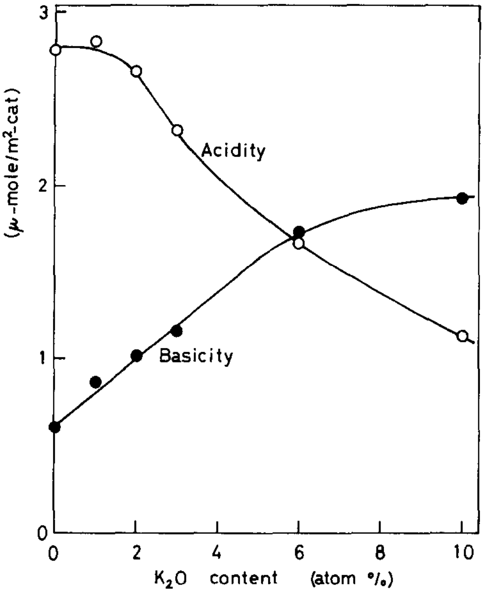

FIG. 1. Acidity and basicity of Co_3O_4–K_2O as a function of the K_2O content.

excess of air was investigated. In seeking a universal rule, the oxidation activity for a variety of organic compounds was tested.

A. Oxidation of n-hexane. For convenience in the experimental procedures, *n*-hexane was chosen as a model paraffinic hydrocarbon. The oxidation was carried out at 200 to 250°C, while changing the amounts of the catalyst from 2 to 20 g.

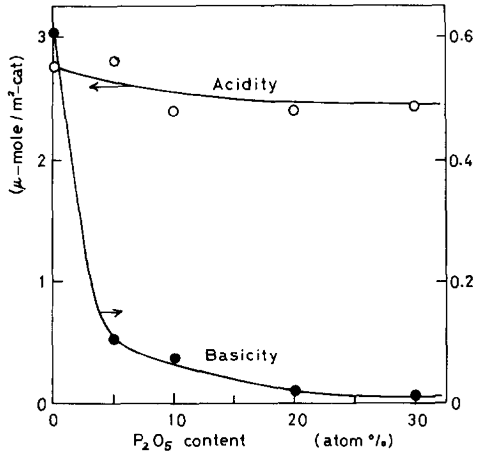

FIG. 2. Acidity and basicity of Co_3O_4–P_2O_5 as a function of the P_2O_5 content.

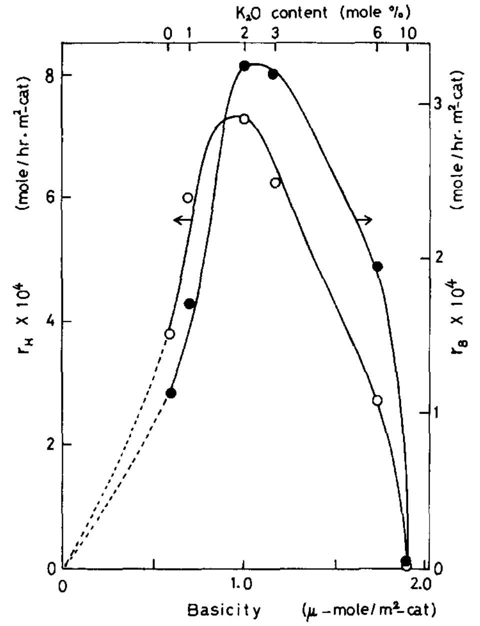

FIG. 3. Relation between the basicity of the Co_3O_4–K_2O catalysts and the oxidation activities for *n*-hexane and 1-butene. (○) r_H: Rate of *n*-hexane oxidation at 230°C, n-C_6H_{14} = 0.39 mole% in air; (●) r_B: Rate of 1-butene oxidation at 215°C, C_4H_8 = 0.67 mole% in air.

The main product was CO_2. The amounts of CO were less than one-twentieth of those of CO_2, and the formation of the other products were negligibly small. The initial rates of CO_2 formation at 230°C for the Co_3O_4–K_2O catalysts and at 250°C for the Co_3O_4–P_2O_5 catalysts, r_H (mole/hr·m^2-catalyst), were measured for each catalyst. Following the principle of the differential reactor, the conversion was held at a low level. The rates are plotted as a function of the basicity of the catalysts in Figs. 3 and 4.

In the case of the Co_3O_4–K_2O catalysts (Fig. 3), the oxidation activity first increases with the basicity, passes through a maximum at about K = 2 atom%, and then decreases sharply with a further increase in the K_2O content. However, in the case of the Co_3O_4–P_2O_5 catalysts (Fig. 4), the activity decreases steadily with a decrease in the basicity.

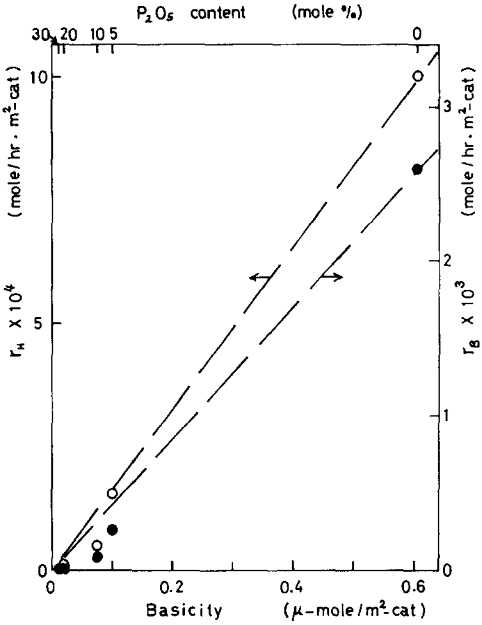

FIG. 4. Relation between the basicity of the Co_3O_4–P_2O_5 catalysts and the oxidation activities for n-hexane and 1-butene. (○) r_H: Rate of n-hexane oxidation at 250°C, n-C_6H_{14} = 0.39 mole% in air; (●) r_B: Rate of 1-butene oxidation at 265°C, C_4H_8 = 0.67 mole% in air.

B. Oxidation of 1-butene. 1-Butene was chosen as an electron-donating (basic) reactant, and it was oxidized. The main product was CO_2. The amounts of butadiene and acids were negligibly small. The initial rates of CO_2 formation at 215°C for the Co_3O_4–K_2O catalysts and at 265°C for the Co_3O_4–P_2O_5 catalysts, r_B (mole/hr·m²-catalyst), were measured for each catalyst. The rates are also plotted in Figs. 3 and 4. The oxidation activity for butene varies in a manner quite similar to the activity for n-hexane in the cases of both Co_3O_4–K_2O and Co_3O_4–P_2O_5.

C. Oxidation of phenol. Phenol was chosen as an acidic reactant, and it was oxidized. The main product was CO_2. The initial rates of CO_2 formation at 265°C for the Co_3O_4–K_2O and at 296°C for the Co_2O_4–P_2O_5 system, r_0 (mole/hr·m²-catalyst), were measured. They are shown as a function of the basicity of the catalysts in Figs. 5 and 6.

In the case of the Co_3O_4–K_2O catalysts (Fig. 5), as long as the K_2O content is not high ($K < 3$ atom%), the oxidation activity increases with an increase in the basicity. However, when the K_2O content is higher than 3 atom%, the activity decreases a little with the basicity. The activity of the Co_3O_4–P_2O_5 decreases steadily with a decrease in the basicity.

D. Oxidation of methanol. The oxidation activity for methanol was studied. Methanol was more reactive than the three other reactants, and the main product was also CO_2. The initial rates of CO_2 formation at 180°C for the Co_3O_4–K_2O system and at 230°C for the Co_3O_4–P_2O_5 system, r_M (mole/hr·m²-catalyst), were measured. The results are also plotted in Figs. 5 and 6. The oxidation activity is correlated well

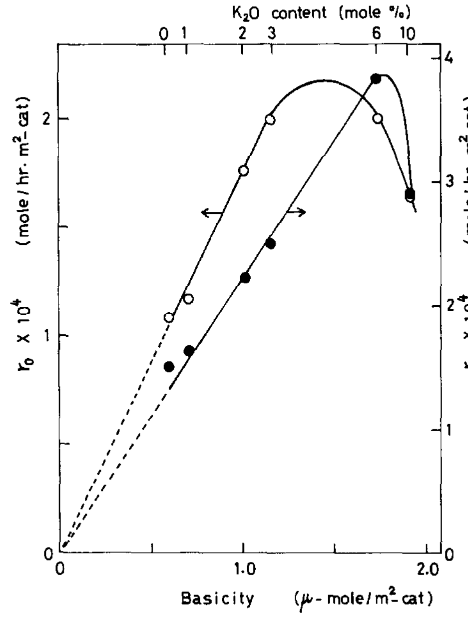

FIG. 5. Relation between the basicity of the Co_3O_4–K_2O catalysts and the oxidation activities for phenol and methanol. (○) r_0: Rate of phenol oxidation at 265°C, phenol = 0.53 mole% in air; (●) r_M: Rate of methanol oxidation at 180°C, methanol = 1.7 mole% in air.

with the basicity of the catalysts, except in the case of the K = 10 atom% catalyst.

DISCUSSION

The generation of a marked acidic property was not observed upon addition of a small amount of P_2O_5 to Co_3O_4, whereas a strikingly high acidic property was generated by the addition of even a very small amount of P_2O_5 to such acidic oxides as MoO_3, WO_3, U_3O_8, and TiO_2. These findings are in line with the results obtained in previous works (*7, 21, 22*). It may be advanced, as a general rule, that the addition of P_2O_5 or MoO_3 to such basic oxides as Bi_2O_3, ZnO, Co_3O_4, NiO, and CuO always decreases the basicity, but it cannot generate the acidic sites as long as the amounts of the additives are small. Probably, the acidic property of the additives is completely extinguished by the basic components.

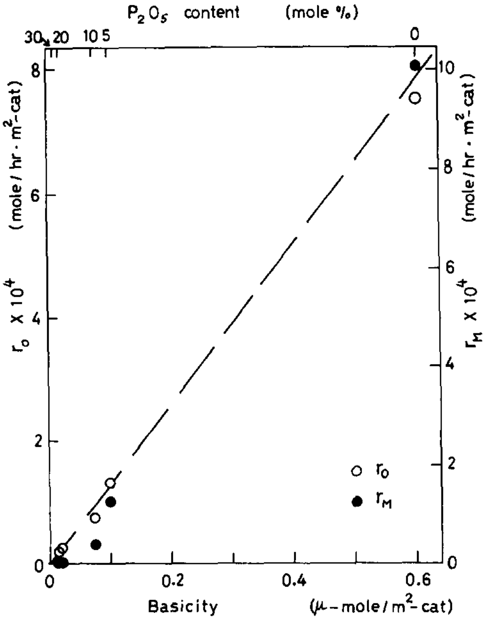

FIG. 6. Relation between the basicity of the Co_3O_4–P_2O_5 catalysts and the oxidation activities for phenol and methanol. (○) r_0: Rate of phenol oxidation at 296°C, phenol = 0.53 mole% in air; (●) r_M: Rate of methanol oxidation at 230°C, methanol = 1.7 mole% in air.

It is characteristic of the Co_3O_4-based catalysts that the oxidation activity is extremely high and that the main product is CO_2 (i.e., no partially oxidized compounds can be obtained, regardless of the reactants), and also that the difference in the activity, depending on the difference in the kind and/or nature of the reactant molecule, is very small compared to that in the cases of mild oxidation catalysts, such as V_2O_5-, MoO_3-, WO_3-, and Bi_2O_3-based oxides (*5, 6*). For example, *n*-hexene can be sufficiently oxidized at about 250°C over the Co_3O_4-based catalysts, much like 1-butene. In addition, no correlation exists between the acidity of the catalysts and the oxidation activity for a basic reactant such as butene. This evidence confirms the validity of the hypothesis that the oxidation activity of the Co_3O_4-based catalysts is governed by the intrinsic oxidation activity rather than by the activation of the reactant molecule.

In both the Co_3O_4–K_2O and Co_3O_4–P_2O_5 systems, as long as the K_2O content is not high, the catalytic activity for the oxidation of each of the four compounds tested here increases with an increase in the basicity of the catalyst. This finding indicates that the intrinsic oxidation activity is dependent on the basicity. In addition, the interrelationship suggests that, when the kind of additive is fixed and the amount is not large, the change in the amount of the additive causes a change in the number, but not a great change in the nature, of the sites. That is, f(M–O and the base strength) in Eq. (3) remains almost constant. Thus, the rate may be written as:

$$\text{Oxidation rate} \propto (\text{basicity}). \qquad (4)$$

In the case of the Co_3O_4–K_2O catalysts containing more than 3 atom% K_2O, the oxidation activities for *n*-hexane and butene decrease with an increase in the basicity of the catalysts (Fig. 3). These results can be explained by assuming that, when the content of K_2O is high, the nature of the active sites is modified by the K_2O, which by itself has no oxidizing power; also, probably the oxidizing power, i.e., the function iv, of the catalysts is suppressed. For example, by the addition of 10 atom% K_2O, the number of basic sites is enhanced, but the oxidizing power of the sites is strongly suppressed.

On the basis of these findings, it seems possible that the oxidation activities for *n*-hexane and butene, shown in Fig. 3, reflect the real features of the intrinsic oxidation activity, which is defined as the combination of functions iii and iv.

From the results shown in Fig. 5, another question arises as to why the oxidation activities for phenol and methanol are not suppressed as strongly as the activities for the hydrocarbons upon the addition of more than 3 atom% K_2O, but remain still active even upon the addition of 6 to 10 atom%. This may also be understood by taking into consideration the facts that an acidic reactant such as phenol can be activated by the basic sites and that the oxidation of methanol to CO_2 is catalyzed by the basic sites, too (*23*). As has been mentioned above, when the K_2O content is high, the oxidizing power becomes weak, but the ability for the activation of the acidic reactant becomes prominent. In the cases of such catalysts, the oxidation activity for an acidic reactant is governed, to a considerable extent, by the activation of the reactant molecule by the basic sites. It may, therefore, be considered that the high oxidation activity at a high K_2O content ($K > 3$ atom%) does not reflect the intrinsic oxidation activity.

In summary, it can be said that, when the amounts of additives are small, the oxidation activity of the Co_3O_4-based catalysts for various types of reactants reflects the intrinsic oxidation activity, and the intrinsic oxidation activity is governed by the basic property of the metal oxide catalysts.

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