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The Acid–Base Properties of MoO_3–Bi_2O_3–P_2O_5 Catalysts and Their Correlation with Catalytic Activity and Selectivity

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The amounts of both the acidic and basic sites of MoO_3-Bi_2O_3-P_2O_5 catalysts over a full range of Bi/Mo ratios were measured by studying the adsorption of basic and acidic molecules, respectively, in the gas phase. The results obtained by the pulse method agreed well with those obtained by the static method. The acidity of pure Bi_2O_3 is far lower than that of MoO_3–P_2O_5, and with an increase in the Bi_2O_3 content, the acidity rapidly increases at first, passes through a maximum at the Bi/Mo atomic ratio of 0.1–0.2, and then decreases. On the other hand, the basicity of MoO_3–P_2O_5 is fairly low compared with that of pure Bi_2O_3; the basicity of the catalyst gradually increases with the Bi_2O_3 content. The relationship between the acid–base properties obtained here and the catalytic behavior obtained previously was investigated. The oxidation and isomerization activities for olefins are proportional to the acidity of the catalyst, and the oxidation activity for an acidic compound and hydrogen is connected with the basicity. The selectivity of the catalyst was also interpreted in connection with the acid–base properties. Finally, the characters of the active sites were discussed, together with those of the acidic and basic sites.

INTRODUCTION

A great number of studies have been made on oxidation over the MoO_3–Bi_2O_3 catalyst system because of its excellent selectivity for the so-called allylic oxidation of olefins, as has been reviewed in recent publications (*1–3*). However, the functions of the catalyst have not yet been firmly established; it is still obscure why such combinations as MoO_3–Bi_2O_3, Fe_2O_3–Sb_2O_5, UO_3–Sb_2O_5, and CuO–SeO_2 display high selectivity; also it has not been fruitful to associate the catalytic behavior with the physicochemical properties common to every metal oxide.

We focused our attention on the fact that MoO_3 is a typical acidic metal oxide, while Bi_2O_3 is a basic metal oxide; the MoO_3–Bi_2O_3 system is a combination of these two oxides with opposite characteristics. Studies of the oxidations over MoO_3–Bi_2O_3–P_2O_5 catalysts with different Bi_2O_3 contents have led us to conclude that the activities and the selectivities in the oxidations are governed by the acid–base properties between the catalyst and the reactant (*4–7*). This acid–base conception has also been found to be good for explaining the results of oxidation over such acidic-type catalysts as MoO_3–P_2O_5 (*8*), V_2O_5–MoO_3 (*9*), and V_2O_5–P_2O_5 (*10*).

The acidic and basic properties of metal oxides have been determined systematically by Tanabe *et al.* (*11–14*) by titration using certain indicators when the solids were not colored. However, in the case of the catalysts used for oxidations consisting mostly of transition-metal oxides, the titration method cannot be used because of their colors and their very small surface areas. Thus, there have been very few studies dealing with these catalysts. For this reason, we used, in our previous studies, the catalytic activity for the dehydration of isopropyl alcohol (IPA) to propylene as a measure of the acidity of the catalyst (*5–10,15*) and the (dehydrogenation rate)/(dehydration rate) ratio in the reaction of IPA as a measure of the basicity (*7,15*), assuming that the dehydration is catalyzed at acidic sites and that the dehydrogenation is catalyzed at both acidic and basic sites. The question, therefore, rises whether these measures of acidity and basicity obtained from the catalytic activities for IPA really represent their true values.

In the present work, we attempted to determine directly both the acidity and the basicity of MoO_3–Bi_2O_3–P_2O_5 catalysts over a full range of Bi/Mo compositions and to establish more firmly the concept that the catalytic activity and selectivity in mild oxidations can be well interpreted in terms of the acid–base properties between the catalyst and the reactant.

EXPERIMENTAL METHODS

Catalyst

The catalysts used in these studies were a series of the MoO_3–Bi_2O_3–P_2O_5 system, with 13 different Bi/Mo ratios and a constant P/Mo ratio (P/Mo = 0.2 atomic ratio). They were the same as those used in the previous works (*4–7*). The surface areas of these catalysts were measured by the BET method; they are listed in Table 1.

Acidity and Basicity Measurements

The acidity and basicity of the MoO_3–Bi_2O_3–P_2O_5 catalysts were measured by the adsorption of basic and acidic molecules, respectively, in the gas phase. The following two methods were used for the sake of comparison.

1. Static method. NH_3 and CO_2 were chosen as the basic and acidic adsorbates, respectively. The adsorption measurements were carried out using an ordinary BET apparatus modified to measure low area. About a 20-g portion of the catalyst was put in an adsorption vessel (about 25 ml) and heat treated in an electric furnace at 500°C for 2 hr under a stream of dried air (50–200 ml/min) injected from a fine steel pipe inserted into the bottom. Immediately after the vessel had been taken out of the furnace, it was quickly connected to the adsorption apparatus and pumped until the catalyst had been cooled to room temperature (about 30 min). A known amount of NH_3 or CO_2 was introduced into the adsorption vessel, and then it was allowed to stand for 20 min before the pressure changes were read. Care was taken to adjust the amount of adsorbates in such a way that the final pressure became around 300 mm Hg. Subsequently, the catalyst

TABLE 1

SURFACE AREA OF THE MoO_3–Bi_2O_3–P_2O_5 CATALYSTS USED

Composition[a] Bi/Mo (atom ratio)	Surface area (m^2/g)	Composition[a] Bi/Mo (atom ratio)	Surface area (m^2/g)
0	1.1	0.7	1.3
0.05	1.3	1.0	1.0
0.10	1.1	2	1.4
0.15	1.1	4	1.3
0.2	1.7	9	1.5
0.3	1.7	∞	1.0
0.4	1.6		

[a] P/Mo = 0.2 (atomic ratio).

was pumped for 30 min at the same temperature. Similar adsorption procedures were then repeated, and the amount of the readsorption was measured. The amount of NH_3 or 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 acidity or basicity of the catalysts.

2. *Gas Chromatographic pulse technique.* 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 length and 4 mm i.d.). The catalyst (1.0 or 1.5 g) was packed in the U-tube and heat treated in a stream of air at 500°C for 2 hr. Immediately after the U-tube had been taken out of the furnace, it was quickly connected to the gas chromatographic column and placed in another furnace kept at 130°C. Then the carrier gas (He: 50 ml NTP/min) was introduced into the system.

Phenol has usually been used as the acidic adsorbate. In this case, a relatively high temperature (above 200°C) is necessary to the measurement, since the boiling point of phenol is high (180°C). In the case of oxidation catalysts, however, the decomposition of phenol cannot be avoided at this temperature. Therefore, it is necessary to use adsorbates with lower boiling points. In the present work, pyridine and acetic acid were chosen as the basic ad and acidic adsorbates, respectively, and the adsorption measurements were performed at 130°C.

A sequence of the pulses of either an *n*-hexane solution of 0.25 *M* pyridine or an *n*-heptane solution of 1.0 *M* acitic acid was injected into the U-tube by means of a microliter injector at intervals of about 2 min. The volume of a pulse was 5–50 μ-l, which was adjusted to be about one-tenth of the total adsorption amount obtained by preliminary measurements. The adsorbate uptake was obtained from the gas chromatographic analysis both at the inlet and at the exit of the U-tube. The peak of the adsorbate at the exit is not observed upon the initial injections, while as the number of pulse increases, the catalyst is saturated with the adsorbate, 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 readsorbed amount 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 acidity or basicity of the catalysts.

RESULTS

Acidity

The acidity of the MoO_3-Bi_2O_3-P_2O_5 catalysts, as determined by the amount of the basic molecules irreversibly adsorbed, is plotted as a function of the Bi_2O_3 content in Fig. 1. A very good parallelism was found between the amount of NH_3 obtained by means of the static method and those of pyridine obtained by means of the

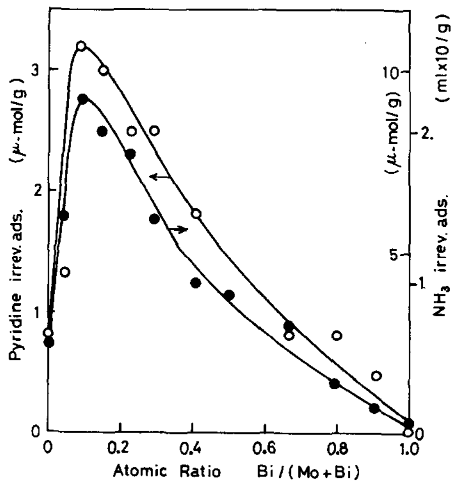

FIG. 1. Acidity of MoO_3-Bi_2O_3-P_2O_5 as a function of the Bi_2O_3 content (●) NH_3 (static method); (○) pyridine (pulse method).

pulse method, which may reflect the validity of these results, although the absolute value of NH_3 was much higher than that of pyridine. The difference, as generally considered, may be attributed to the differences in both the base strength and molecular size between NH_3 and pyridine. Further investigation is, however, necessary to clarify the natures of the acidic sites, such as the distribution of the acid strength and the structure.

It is evident at least that the acidity of pure Bi_2O_3 is far lower than that of MoO_3–P_2O_5 and that, with an increase in the Bi_2O_3 content of the catalyst, the acidity rapidly increases at first, passes through a maximum at the Bi/Mo atomic ratio of 0.1–0.2, and then decreases to the value of the pure Bi_2O_3 catalyst. It should be noted that a new acidic site is generated by adding a small amount of such a basic element as Bi_2O_3 (as described below) to MoO_3–P_2O_5. All these results are consistent with those obtained previously from the IPA dehydration activity (*5–7*).

Basicity

The basicity of MoO_3–Bi_2O_3–P_2O_5 catalysts determined by the irreversible adsorption of acidic molecules in the gas phase is shown in Fig. 2. A parallel was also found between the amount of CO_2 obtained by means of the static method and that of acetic acid obtained by means of the pulse method. This fact supports the validity of the data.

The results indicate that the basicity of MoO_3–P_2O_5 (1–0.2) is fairly low compared with that of pure Bi_2O_3, and that the basicity of MoO_3–Bi_2O_3–P_2O_5 gradually increases with an increase in the Bi_2O_3 content and increases sharply with the Bi_2O_3 content at Bi/Mo > 2; in other words, the basicity of Bi_2O_3 sharply decreases upon the addition of a small amount of such an acidic element as MoO_3–P_2O_5. These results are consistent with those obtained previously from the (dehydrogenation rate)/(dehydration rate) ratio in the reaction of IPA (*7*).

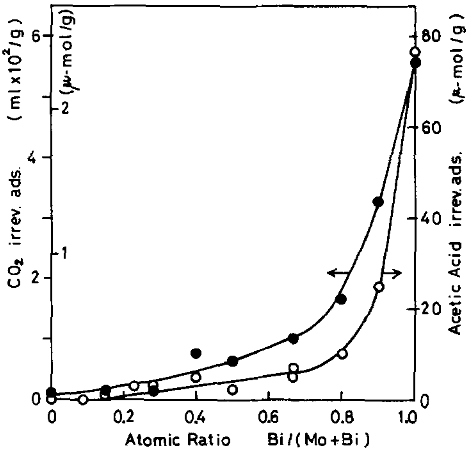

FIG. 2. Basicity of MoO_3–Bi_2O_3–P_2O_5 as a function of the Bi_2O_3 content: (●) CO_2 (static method); (○) acetic acid (pulse method).

DISCUSSION

I. Correlation between Catalytic Activities and Acid–Base Properties

On the basis of the acid–base properties obtained here and the catalytic behavior established previously (*4–7*), the relationship between the catalytic activities and the acid–base properties was investigated.

A. Isomerization activity for butene. The (*trans*-2-C_4H_8 + 1-C_4H_8)/(*cis*-2-C_4H_8 + *trans*-2-C_4H_8 + 1-C_4H_8) ratio was employed as a measure of the isomerization activity for *cis*-2-butene; it is plotted as a function of the acidity, i.e., the amount of NH_3 irreversibly adsorbed, in Fig. 3. A proportional relationship was obtained between the isomerization activity and the acidity of the catalyst. This evidence reveals that the active sites for the isomerization are ascribable to the acidic sites.

B. Oxidation activity for olefin. The relative oxidation activities of catalysts should differ largely according to whether the reactant is acidic or basic, and whether the

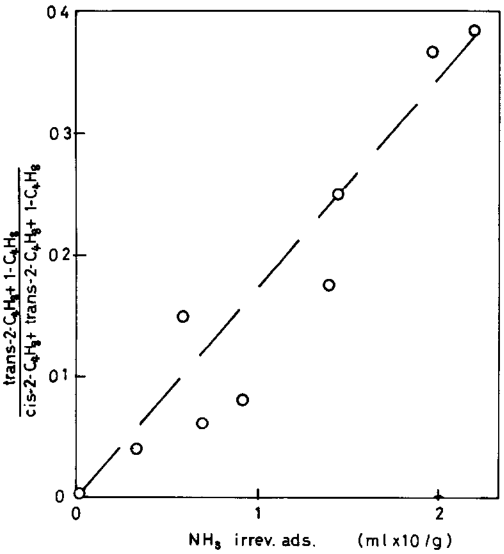

FIG. 3. Relation between the isomerization activity for *cis*-2-butene and the acidity: acidity = amount of NH_3 irreversibly adsorbed; isomerization = 350°C, contact time of 0.8 sec, 0.67 mol% *cis*-2-C_4H_8 in air.

oxygen is present in an excess or is deficient.

Butadiene was chosen as the electron-donor-type (basic) reactant, and its overall consumption in the presence of excess oxygen was taken as the oxidation activity, which is plotted as a function of the acidity of the catalyst in Fig. 4. A relatively good proportional relationship was obtained between the oxidation activity and the acidity. No correlation with the basicity was found. This fact indicates that, under such oxygen-rich conditions, the oxidation rate of basic reactants such as olefins is controlled at a step which is catalyzed only by acidic sites.

C. Oxidation activity for acidic compound. Maleic anhydride was chosen as the acidic reactant, and the oxidation activity for it in the presence of excess oxygen is plotted as a function of the basicity of the MoO_3-Bi_2O_3-P_2O_5 catalyst, i.e., the volume of CO_2 irreversibly adsorbed in Fig. 5. The activity increases with an increase in the basicity. This fact indicates that the basic sites of the catalyst play an important role in the oxidation of acidic compounds. The basic sites may relate to either the activation sites for an acidic reactant or the oxidizing sites (as described below). However, the evidence that the activity for acid oxidation increases and becomes very high even with a

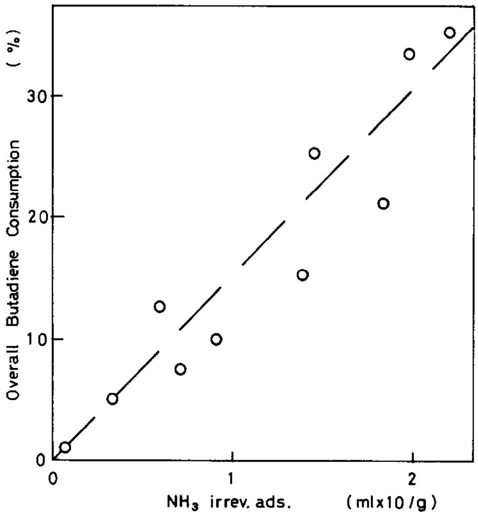

FIG. 4. Relation between the oxidation activity for butadiene and the acidity: acidity = amount of NH_3 irreversibly adsorbed; oxidation = 400°C, contact time of 0.8 sec, 0.67 mol% C_4H_6 in air.

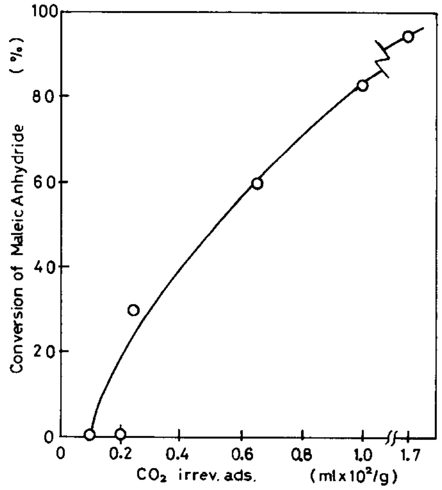

FIG. 5. Relation between the oxidation activity for maleic anhydride and the basicity: basicity = amount of CO_2 irreversibly adsorbed; oxidation = 400°C, contact time of 0.8 sec, 0.7 mol% maleic anhydride in air.

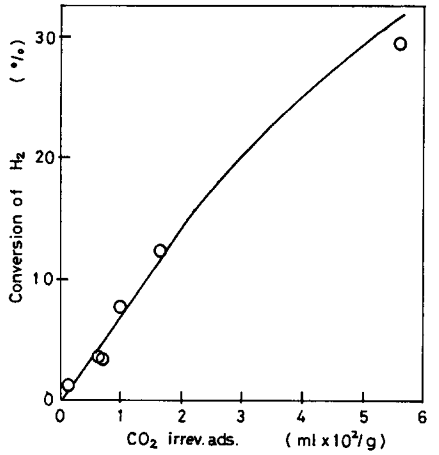

FIG. 6. Relation between the oxidation activity for hydrogen and the basicity: basicity = amount of CO_2 irreversibly adsorbed; oxidation = 450°C, contact time of 0.8 sec, 3.0 mol% H_2 in air.

small increase in the basicity may imply the importance of the former.

D. Intrinsic oxidation activity. It has been established that hydrogen and paraffinic hydrocarbons act upon metal oxide catalysts, more or less, as electron-donating reagents. However, this tendency might be so weak that the activity for the combustion of these compounds is really governed by the intrinsic oxidation activity of the surface rather than by the activation of the reactants (*16*). In addition, it has been proposed that the chemisorption of hydrogen occurs on oxide ions, not on cations (*17*).

In Fig. 6 the oxidation activity for hydrogen in the presence of excess oxygen is plotted as a function of the basicity, i.e., the volume of CO_2 irreversibly adsorbed. The conversion of hydrogen increases almost proportionally to the basicity of the catalyst. This indicates that the intrinsic oxidation activity is associated with the basic sites of the catalyst.

II. Correlation between Selectivity and Acid-Base Properties

The MoO_3–Bi_2O_3–P_2O_5 catalysts may be classified into three groups in terms of their acid-base properties or their Bi_2O_3 content. The characteristics of each group are listed in Table 2.

The selective oxidation for such basic reactants as olefins can be classified into two groups on the basis of the acid-base properties of the product:

Type 1: basic reactant → acidic product,

Type 2: basic reactant → basic product.

The formation of maleic anhydride from butadiene, in an excess of air, was chosen as a reaction of Type 1, and the formation of butadiene from butene, as a reaction of Type 2. The selectivities for these two reactions are plotted as a function of the Bi_2O_3 content in Fig. 7.

It is evident for two reasons that one requirement for an effective catalyst for the Type 1 reaction is the acidic property:

1. The acidic catalyst is active for the reactant;
2. The acidic catalyst is inactive for the degradation of the acidic compound produced. Therefore, the catalysts of Group I are favorable for the Type 1 reaction.

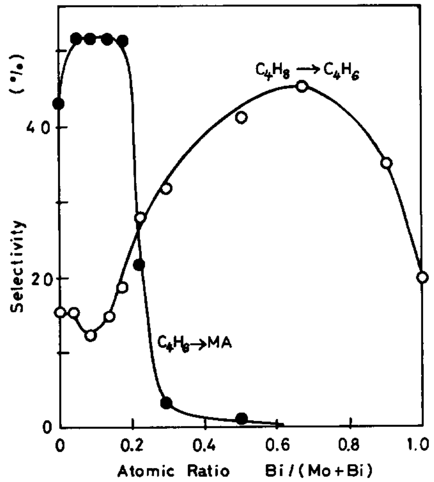

FIG. 7. Selectivity versus Bi/(Mo + Bi) ratio: (●) selectivity of C_4H_6 to maleic anhydride, conversion = about 80%, 0.67 mol% C_4H_6 in air; (○) selectivity of C_4H_8 to C_4H_6, conversion = about 50%, 0.67 mol% C_4H_8 in air.

TABLE 2
CHARACTERS OF MoO_3-Bi_2O_3-P_2O_5 CATALYSTS

Group	Composition Bi/Mo	Type of catalyst	Acidity	Basicity	Oxidation activity for Olefin	Oxidation activity for Acid	Oxidation activity for Hydrogen	Selectivity for reaction of
I	0–0.3	Acidic	High	Low	High	Low	Low	Base → acid
II	0.5–3	Sohio	Medium	Medium	Medium	Medium	Low	Base → base
III	≥ 4	Basic	Low	High	Low	High	High	(None)

On the other hand, for the Type 2 reaction, it is found that both the acidity and the basicity should be present in proper quantities; too high an acidity or basicity decreases the selectivity. It seems plausible that the presence of the acidic character is desirable in enhancing the activity for the reactant; however, when the acidic character is too high, the reaction cannot stop at the step of butadiene, because it is oxidized more rapidly than butene. On the other hand, when the catalyst is too basic and the acidity is too low, the activity for the reactant is very low, and so the oxidation under severe conditions proceeds nonselectively until the combustion is completed. Therefore, the catalysts of Group II, i.e., Sohio-type catalysts, are favorable for the Type 2 reaction. The catalysts of Group III are improper for selective oxidation.

III. Active Sites and Acid-Base Sites

Let us now discuss the characters of the active sites in connection with the acidic and basic sites. The acidic sites in metal oxides generally consist of metal cations with a specifically high electron affinity due to the particular influence of adjacent ions (*11*), though their structure and mechanism of generation have not been fully explained. In the case of the MoO_3-Bi_2O_3 or MoO_3-Fe_2O_3 system, they can reasonably be ascribed to special Mo^{6+} ions rather than to the Bi^{3+} or Fe^{3+} ions, since the Mo^{6+} ion is much more electronegative than the Bi^{3+} or Fe^{3+} ions. The Mo^{5+} signal observed in the reduction of MoO_3-based catalysts with olefin (*17,18*) may reflect the acidic character of the catalysts. The anion vacancies or B-centers proposed by Batist *et al.* (*19*) and Matsuura and Schuit (*20*), and the $Mo(O_t)_3$ species proposed by Mitchell and Trifiro (*21*) may be based on the same notion as that of acidic sites, though we have no proof on the basis of which to discuss their opinions in detail.

As regards the catalytic action, it has been considered by many investigators, but only for "Sohio-type catalysts" (Bi/Mo = 2/3–2), that such electron-donor-type reactants as olefin first interact with the acidic sites of the catalyst (Mo^{6+}) and that the electron of the olefin may be localized on a certain metal cation to form a slightly positively charged π-complex and a metal ion of a reduced state. This first step is followed by a second step: the abstraction of an allylic hydrogen atom to form an allylic intermediate; this second step is the rate-determining one.

However, the evidence that the acidity is the sole factor deciding the activity of both the oxidation and isomerization of olefin (Figs. 3 and 4) may imply that the hydrogen atom is abstracted by Lewis-type acidic sites, probably as the hydride ion (H^-), without the direct participation of active oxidizing species, namely, basic sites (discussed below). This view is different from that of many investigators.

Whether the acidic sites act as electron-abstractors or as hydrogen-abstractors from olefin, the availability for the activation of olefin may be connected with the acid strength of the sites; therefore, the higher the acid strength, the higher the availability. Thus, the rates of the oxidation and isomerization can be expressed as:

$$r \propto (\text{acidity} \cdot f(\text{acid strength}), \qquad (1)$$

where (acidity) is the number of active sites and *f*(acid strength) is the activity of a site.

Though the acid strengths have not been measured here, it may be presumed that, when the kind of each component is fixed in a mixed oxide catalyst, the change in the composition, i.e., the Bi/Mo ratio, causes a change in the number of the acidic sites, but not a great change in the nature of the sites (*11*). That is, the function of the acid strength in Eq. (1) may be almost constant in a mixed system. Thus, the rate may be written as:

$$r \propto (\text{acidity}). \qquad (2)$$

This may be observed in practice in Figs. 3 and 4.

In the case of MoO_3-rich catalysts ($Bi/Mo < 0.3$), the kinetics of the oxidation is of nearly the 0.5 order with respect to the oxygen concentration (*5*). This dependence of the rate on the oxygen concentration may be interpreted, as Batist *et al.* (*19*) did, in terms of the speculation that the gas or adsorbed oxygen serves to return the reduced acid site to its oxidized state and so keep the acidic character.

The nature of the basic site is discussed next. It has been reported by several workers (*12*,*13*,*22*) that a large part of the basic sites determined by the adsorption of acidic substances consist of surface lattice oxygen, O^{2-}. On the other hand, Keulks (*23*) and Wragg *et al.* (*24*) have reported that the active oxygen species available for oxidation is lattice oxygen, O^{2-} ions.

These views allow us to infer that, in the case of an oxidation catalyst, a basic site, O^{2-}, has two aspects:

1. Action as a proton abstractor or electron donor, which is essential for all basic compounds, such as MgO, CaO, and StO;
2. Action as an oxidizing reagent, which arises only when the lattice oxygen species is mobile.

Therefore, in the case of oxidation catalysts, the basicity represents the amount of oxygen species available for oxidation as well as that of the electron-donating site. The mobility of this oxygen species may be connected with the metal–oxygen bond strength.

The intrinsic oxidation activity of a catalyst may depend on two factors: (a) the number of oxidizing sites, i.e., the basicity, and (b) the activity of a site, i.e., the metal–oxygen bond strength, M–O. Thus, it may be expressed as:

$$\text{intrinsic oxidation activity} \propto (\text{basicity}) \cdot \text{f(M–O)}. \qquad (3)$$

It may be presumed also that, when the kind of each component is fixed in a mixed oxide system, a change in the composition causes a change in the amount of an active site, but not a great change in the nature of the site. That is, the function of M–O in Eq. (3) may be almost constant in a mixed system. Thus, activity may be written as:

$$\text{intrinsic oxidation activity} \propto (\text{basicity}). \qquad (4)$$

This may be observed in practice in Fig. 6.

It seems that, in such binary systems as MoO_3–Bi_2O_3, MoO_3–Fe_2O_3, Sb_2O_5–Fe_2O_3, Sb_2O_5–UO_3, SeO_2–CuO, and As_2O_3–Fe_2O_3, the role of the components of a lower electronegativity is connected with the basic sites of the catalysts and that the A-centers proposed by Matsuura and Schuit (*20*) are substantially the same as the basic sites.

In the oxidation of olefin, the oxygen species of basic sites probably participate only in such a step as a nucleophilic addition of an oxygen anion to positively charged intermediates, and this step is fast. Therefore, the rate becomes independent of the basicity. This idea accords with the experimental results.

On the other hand, in the case of the oxidation of acidic reactants, it may be presumed that the reactants interact on basic sites with a high affinity for acidic compounds and that, then, they are activated in certain manners.

With regard to the catalytic behavior for ammoxidation, whose correlation with the phase change of the catalysts has been reported by Aykan (*25*) and Kuczynski and Carberry (*26*), the acid–base conception may be still effective in explaining it.

In conclusion, it should be emphasized that the activity and selectivity in mild oxidation can be well interpreted in connection with the acid–base properties of catalysts. The acidic sites contribute to the activation of electron-donor-type reactants such as olefins and the basic sites are connected with the oxidizing sites. The combination of the metal oxides contributes to the modification of both the acidic and basic properties of a catalyst.

REFERENCES

1. Hucknall, D. J., "Selective Oxidation of Hydrocarbons." Academic Press, London, 1974.

2. Sachtler, W. M. H., *Catal. Rev.* **4,** 27 (1970).

3. Voge, H. H., and Adams, C. R., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 17, p. 151. Academic Press, New York, 1967.

4. Ai, M., and Suzuki, S., *J. Catal.* **26,** 202 (1972).

5. Ai, M., and Suzuki, S., *Shokubai* **14,** 50p (1972).

6. Ai, M., and Suzuki, S., *Bull. Chem. Soc. Jap.* **46,** 321, 1208 (1973).

7. Ai, M., and Suzuki, S., *Bull. Jap. Petrol. Inst.* **16,** 118 (1974).

8. Ai, M., and Suzuki, S., *J. Catal.* **30,** 362 (1973).

9. Ai, M., and Suzuki, S., *Nippon Kagaku Kaishi* **1973,** 260.

10. Ai, M., and Suzuki, S., *Bull. Chem. Soc. Jap.* **47,** 3074 (1974).

11. Shibata, K., Kiyoura, T., Kitagawa, J., Sumiyoshi, T., and Tanabe, K., *Bull. Chem. Soc. Jap.* **46,** 2985 (1973); **47,** 1064 (1974).

12. Tanabe, K., and Saito, K., *J. Catal.* **35,** 247 (1974); *Nippon Kagaku Kaishi* **1973,** 1845; **1974,** 1014.

13. Mohri, M., Tanabe, K., and Hattori, H., *J. Catal.* **32,** 144 (1974).

14. Itoh, M., Hattori, H., and Tanabe, K., *J. Catal.* **35,** 225 (1974).

15. Ai, M., and Suzuki, S., *Shokubai* **15,** 159p (1973).

16. Sachtler, W. M. H., and De Boer, N. H., *Proc. Int. Congr. Catal., 3rd, 1964* **1,** 252 (1965).

17. Peacock, J. M., Sharp, M. J., Parker, A. J., Ashmore, P. G., and Hockey, J. A., *J. Catal.* **15,** 379 (1969).

18. Krivanek, M., Jiru, P., and Strand, J., *J. Catal.* **23,** 259 (1971).

19. Batist, P. A., Kapteijins, C. J., Lippens, B. C., and Schuit, G. C. A., *J. Catal.* **7,** 33 (1967).

20. Matsuura, I., and Schuit, G. C. A., *J. Catal.* **20,** 19, (1971).

21. Mitchell, P. C. H., and Trifiro, F., *J. Chem. Soc. A* 3183 (1970).

22. Krylov, O. V., Markova, Z. A., Trefiakov, I. I., and Fokina, E. A., *Kinet. Katal.* **6,** 128 (1965).

23. Keulks, G. W., *J. Catal.* **19,** 232 (1970).

24. Wragg, R. D., Ashmore, P. G., and Hockey, J. A., *J. Catal.* **22,** 49 (1971).

25. Aykan, K., *J. Catal.* **12,** 281 (1968).

26. Kuczynski, G. C., and Carberry, J. J., *J. Catal.* **34,** 50 (1974).