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The Relationship between the Oxidation Activity and the Acid–Base Properties of Fe_2O_3-Based Mixed Oxides

I. The Fe_2O_3–V_2O_5 and Fe_2O_3–MoO_3 Systems

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The acidity and basicity of two series of binary oxides, Fe_2O_3–V_2O_5 and Fe_2O_3–MoO_3, with different compositions were directly measured by means of adsorption of basic and acidic molecules from the gas phase, using both static and pulse methods. The acidity of the Fe_2O_3–V_2O_5 catalysts increases steadily with increasing V_2O_5 content, and that of the Fe_2O_3–MoO_3 attains a maximum at Mo = 30–40 at%. The trend of these changes is similar to that observed in the cases of TiO_2 and SnO_2. Fe_2O_3 is more basic than TiO_2 and SnO_2, and the basicity decreases sharply upon the addition of even small amounts of V_2O_5 and MoO_3. In the case of the Fe_2O_3–MoO_3 catalysts, the catalytic activity for the oxidation of butadiene correlates well with the acidity, while the activity of the Fe_2O_3–V_2O_5 increases more sharply than the acidity with the addition of V_2O_5 in the low range of $V < 20$ at%. A high selectivity to maleic anhydride from butadiene is obtained with the acidic catalysts ($V > 30$ at%, $Mo > 10$ at%), and the selectivity to butadiene from 1-butene increases upon the addition of a small amount (2–5 at%) of V_2O_5 or MoO_3, but decreases upon further addition. It can be concluded that the activity and selectivity in the oxidation of olefins can be relatively well interpreted in terms of the acid–base properties of the catalysts, much as in the cases of many other V_2O_5- or MoO_3-containing catalysts.

INTRODUCTION

By itself, Fe_2O_3 is impractical as a catalyst for selective oxidations, though it is somewhat active in oxidations. However, the mixed-oxide system combining Fe_2O_3 with some other oxides are known to be very effective for certain selective oxidations. Fe_2O_3–MoO_3 catalysts are most widely used for the oxidation of methanol to formaldehyde (*1*). The Fe_2O_3–V_2O_5 system (*2*) has been reported to be selective in the oxidation of methanol, much like V_2O_5–MoO_3 (*3*). Fe_2O_3–MoO_3–P_2O_5 catalysts are effective in the ammoxidation of xylenes (*4*). Fe_2O_3–Sb_2O_4 (*5*) and certain ferrite-based compounds (*6*–*8*) have been found to exhibit an excellent selectivity in the oxidative dehydrogenation of *n*-butene to butadiene. Fe_2O_3–As_2O_3 has been proposed for use in the oxidation of propylene to acrolein (*9*). These combinations induce a great change in catalytic behavior. In particular, the characteristic features of the selectivity become quite different as different sorts or amounts of oxides are combined with Fe_2O_3.

What is the role of each component? The reaction mechanisms and the nature of the active sites in each case have been actively investigated. With regard to the oxidation

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of methanol on Fe_2O_3–MoO_3, for instance, the oxidizing agent is believed to be the lattice oxygen (*10, 11*). Trifirò *et al.* postulated that the ability for selective oxidation is connected with the double-bond character of MoO_3 (*12*) and that the role of iron is to transfer water and oxygen between the catalyst surface and the gas phase (*13*). The participation of acidic sites in the reaction was proposed by Jirů *et al.* (*14*) and by Pernicone *et al.* (*15*), by analogy with the behavior of alcohols on such non-oxidation catalysts as Al_2O_3 and SiO_2–Al_2O_3. Pernicone *et al.* (*16*), furthermore, 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.* (*17*) concluded that the selective oxidation is caused by Mo^{6+} ions and that Fe^{3+} ions hinder the reduction of the Mo^{6+} cation and increase the lability of the lattice oxygen available for the oxidation process. Recently, Sala and Trifirò (*18*) stated that Fe_2O_3 is able to adsorb and activate gaseous oxygen and that the role of iron is to make easier the reoxidation of molybdenum ions reduced by the organic molecule.

With regard to acid–base properties, Fe_2O_3, much like TiO_2 and SnO_2, is an acid–base bifunctional catalyst. In addition, these properties are significantly modified by the addition of a small quantity of acidic or basic compounds such as MoO_3, P_2O_5, or K_2O (*19*).

In previous reports (*20–25*), we have proposed, as a general rule, that in the case of mild oxidation the catalytic activity is decided preponderantly by the activation of the organic molecule rather than by that of oxygen, and that these activations may be associated with the possibility of electron transfer, i.e., the acid–base type interaction, between organic molecule and catalyst. The acidic sites, probably consisting of metal ions with a particularly high electron affinity, play a role in the electron transfer from reactant to the sites, resulting in the formation of a cationic intermediate and a reduced metal ion; the acidic sites contribute to the activation of the electron-donating (basic) reactants, such as olefins. On the other hand, the basic sites, because of their electron-donating ability, serve to adsorb and activate the acidic reactants such as carboxylic acids.

The first purpose of the present paper is to demonstrate how the addition of various amounts of V_2O_5 or MoO_3 modify the acid–base properties as well as the oxidation activity and selectivity. The second purpose is to confirm how catalytic behavior is correlated with acid–base properties. The results concerning other sorts of Fe_2O_3-based mixed oxides and the oxidation of methanol will be dealt with in subsequent papers.

EXPERIMENTAL

Catalysts

Two series of Fe_2O_3-based binary oxide catalysts, Fe_2O_3–V_2O_5 and Fe_2O_3–MoO_3, with different compositions were prepared as follows. Aqueous NH_4VO_3 or $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ solutions were added to $Fe(NO_3)_3 \cdot 9H_2O$ solutions and 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 metals. The mixtures were then evaporated to dryness with vigorous stirring. The catalysts were calcined in a stream of air at 500°C for 4–5 hr.

Acidity and Basicity Measurements

The acidity and basicity of the catalysts were determined by studying the adsorption of basic and acidic molecules, respectively, in the gas phase, using both static and pulse methods.

Static method. NH_3 and CO_2 were chosen as the basic and acidic adsorbates, respectively. The amount of adosrption at a pressure of 300 mm Hg was measured volumetrically using an ordinary BET apparatus modified to measure low areas. 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 obtained as the difference between the amount of readsorption and that of the first adsorption. This was adopted as a measure of the acidity or basicity.

Gas chromatographic pulse technique. Butene pulses and pyridine pulses were fed into a U-tube containing 1 g of catalyst (160°C) alternately and separately; the amount of pyridine required to inhibit completely the isomerization of 1-butene was adoped as a measure of the acidity. A sequence of pulses of acetic acid was injected into the U-tube (130°C), and the amount of acetic acid required to saturate the catalyst was evaluated. Subsequently, the carrier gas (He) was allowed to pass through for 30 min at the same temperature. Then the same procedures were repeated, and the amount of readsorption was obtained. The amount irreversibly adsorbed was obtained as the difference between the amount of readsorption and that of the first adsorption; it was adopted as a measure of the basicity. The techniques of the measurements have been described in earlier papers (*20, 21, 23*).

Reaction Procedures

The vapor-phase oxidation of 1,3-butadiene and 1-butene, the isomerization of 1-butene, and the dehydration and dehydrogenation of isoporpyl alochol (IPA) were carried out in an ordinary continuous-flow reaction system. The reactor was a steel tube, 50 cm in length, with a 1.8-cm i.d. The concentrations of butene, butadiene, and IPA were about 0.67, 0.67, and 1.65 mol% in air, unless otherwise indicated. The total flow rate (at 25°C) was kept constant at 1.5 liters/min, and the amount of catalyst was 1–20 g. The exit gas from the reactor was led into four chilled water-scrubbers. At the end of 1 hr, the contents of the scrubbers were collected (about 300 ml) and titrated with 0.1 *N* sodium hydroxide using a pH meter. The yields of maleic anhydride and other acids were calculated from the titration curves. The feed gas and exit gas were analyzed by means of gas chromatography. The experimental procedures were the same as those used previously (*20–26*).

RESULTS

1. Surface Area

The effect of the catalyst composition on the specific surface area was first checked by the BET method using nitrogen at −196°C. The results are shown in Fig. 1. The surface area increases sharply upon the addition of a small amount of V_2O_5 or MoO_3 to Fe_2O_3; it passes through a maximum at about V or Mo = 10 atom% and then decreases again. The trend of these changes is similar to that observed in the

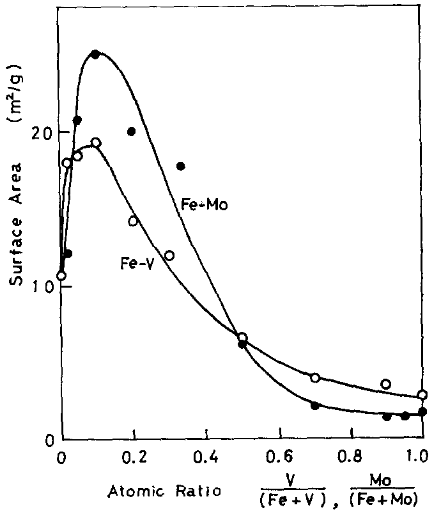

FIG. 1. Effect of the catalyst composition on the specific surface area.

cases of SnO_2- and TiO_2-based oxides (*21–23*).

2. Acidity

The acidity per unit of the surface area of the Fe_2O_3–V_2O_5 and Fe_2O_3–MoO_3 catalysts, as determined by the amount of NH_3 irreversibly adsorbed at 200 and 250°C (static method) and by that of pyridine required to poison completely the isomerization activity for 1-butene at 160°C (pulse method), is plotted as a function of the V_2O_5 or MoO_3 content in Figs. 2 and 3. In the case of MoO_3-rich (Mo > 50 atom%) catalysts, the isomerization activity was too low to measure the amount of pyridine. A parallelism is found between the amounts of NH_3 obtained by the static method and those of pyridine obtained by the pulse method. These parallels prove the validity of these results.

The initial rate of the IPA dehydration in the presence of an excess of air at 175°C, r_p (mol/m² of catalyst), is also plotted in Figs. 2 and 3. The value of r_p varies in the same direction as the acidity. This indicates that the value of r_p is effective enough as a scale of the acidity of the catalysts in the cases of the Fe_2O_3-based catalysts, too.

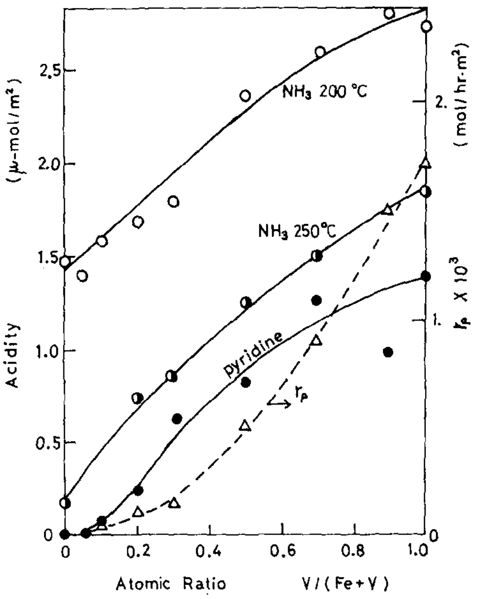

FIG. 2. Acidity of Fe_2O_3–V_2O_5 as a function of the V_2O_5 content: (○) irreversible adsorption of NH_3 at 200°C; (◑) at 250°C; (●) pyridine required to poison the isomerization activity for 1-butene; (△) the dehydration activity for IPA, r_p.

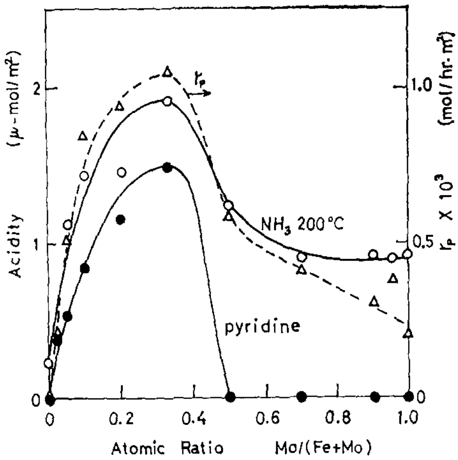

FIG. 3. Acidity of Fe_2O_3–MoO_3 as a function of the MoO_3 content: (○) irreversible adsorption of NH_3 at 200°C; (●) pyridine required to poison the isomerization activity for 1-butene; (△) the dehydration activity for IPA, r_p.

Fe_2O_3 by itself is scarcely acidic, but the acidity increases steadily with the V_2O_5 content much as in the case of the SnO_2–V_2O_5 (*21*) and TiO_2–V_2O_5 systems (*23*). On the other hand, in the case of Fe_2O_3–MoO_3 catalysts, the acidity shows a maximum at about Mo = 30–40 atom% and then decreases again to a low value of pure MoO_3. It is evident at least that new acidic sites are generated by combination with MoO_3, as is also observed in the cases of the SnO_2–MoO_3 and TiO_2–MoO_3 (*22*, *23*). However, it should be noted that the acidity of Fe_2O_3–MoO_3 is fairly low compared with those of SnO_2–MoO_3 and TiO_2–MoO_3.

3. Basicity

The basicity per unit surface area of the Fe_2O_3–V_2O_5 and Fe_2O_3–MoO_3 catalysts, as determined by the amount of CO_2 irreversibly adsorbed at 20°C and by that

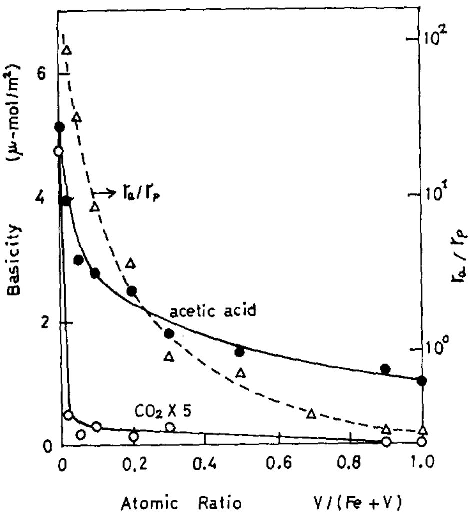

FIG. 4. Basicity of Fe_2O_3–V_2O_5 versus the V_2O_5 content: (○) irreversible adsorption of CO_2 at 20°C; (●) irreversible adsorption of acetic acid at 130°C; (△) the r_a/r_p ratio, $T = 175°C$, IPA = 1.65 mol% in air.

of acetic acid adsorbed at 130°C (pulse method), is plotted as a function of the V_2O_5 or MoO_3 content in Figs. 4 and 5. Parallels were found between the amounts of CO_2 and those of acetic acid. This proves the validity of the results.

The r_a/r_p ratio is also plotted in Figs. 4 and 5, where r_p and r_a are the initial rates of the IPA dehydration and dehydrogenation, respectively, at 175°C. The direction of change in the r_a/r_p ratio is similar to that of the basicity of the catalysts. This indicates that the value of the r_a/r_p ratio is valid enough as a rough index of the basicity much as in the case of MoO_3–Bi_2O_3–P_2O_5 (*20*), SnO_2–V_2O_5 (*21*), SnO_2–MoO_3 (*22*), TiO_2–MoO_3 (*23*), TiO_2–V_2O_5–P_2O_5 (*24*), and WO_3–P_2O_5 (*26*) systems.

Fe_2O_3 by itself is fairly basic compared to SnO_2 and TiO_2, which is in conformity with our earlier results (*19*), and the basicity decreases sharply upon the addition of even a small amount (2–5 atom%) of V_2O_5 or MoO_3. The basic sites originating from Fe_2O_3 may be extinguished by the combination with these acidic compounds, as can reasonably be expected in the case of a liquid acid–base.

4. Isomerization Activity for Butene

The catalytic activity for the isomerization of 1-butene to 2-butenes under the circumstances of the oxidation was also investigated. The reaction was carried out at 225°C by changing the catalyst amount in the 1- to 20-g range, and the rate, r_I (moles per hour and square meter of catalyst), was obtained from the data at low conversion of 1-butene.

The results are plotted as functions of the catalyst composition in Fig. 6. The activity changes in a manner similar to the acidity of the catalysts shown in Figs. 2 and 3. The product ratio of *cis*-/*trans*-2-butene is 1/2. The results support the view proposed in our previous work (*20–26*) that, under circumstances of oxidation, isomerization is catalyzed only by acidic sites and that, consequently, the activity is effective enough as an index of the acidity of the solid catalyst.

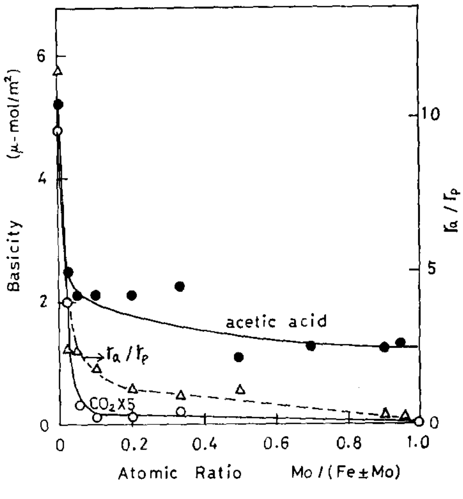

FIG. 5. Basicity of Fe_2O_3–MoO_3 versus the MoO_3 content: (○) irreversible adsorption of CO_2 at 20°C; (●) irreversible adsorption of acetic acid at 130°C; (△) the r_a/r_p ratio.

5. *Oxidation Activity for Olefin*

The oxidation of butadiene in the presence of an excess of air was chosen as the model reaction in the same way as in previous works (*20–25*). The initial rate of the overall consumption of butadiene at 290°C for the Fe_2O_3–V_2O_5 catalysts and at 320°C for the Fe_2O_3–MoO_3 catalysts, r_B (mole/hr·m^2 of catalyst), was adopted as a measure of the oxidation activity for convenience in the experimental procedures. The products at higher total conversion will be mentioned in the next section. The activity is plotted as a function of the catalyst composition in Figs. 7 and 8.

6. *Selectivity in the Oxidation of Olefin*

Since the starting materials of selective oxidations are mostly basic compounds such as olefinic or aromatic hydrocarbons or aldehydes, the reactions can be devided into two types (*19–25*): Type 1, basic reactant → acidic product (acid formation); and Type 2 basic reactant → basic product (basic formation). In a manner similar to those employed in previous studies (*20–25*), the oxidation of butadiene to maleic anhydride in the presence of an excess of air (0.67 mol% of butadiene) was chosen as a Type 1 model reaction. The main products, other than maleic anhydride, were CO_2 and CO. The amount of

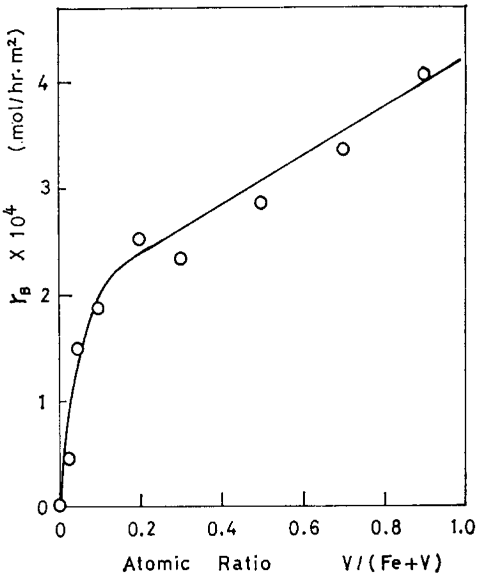

FIG. 7. Oxidation activity for butadiene as a function of the V_2O_5 content: $T=290°C$, butadiene $=0.67$ mol% in air.

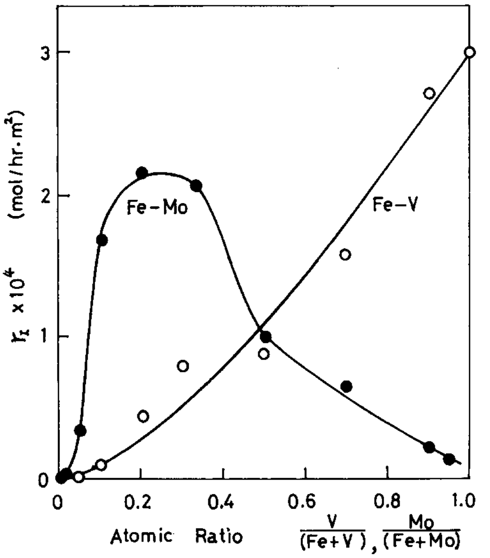

FIG. 6. The isomerization activity for 1-butene at 225°C as a function of the content of V_2O_5 or MoO_3.

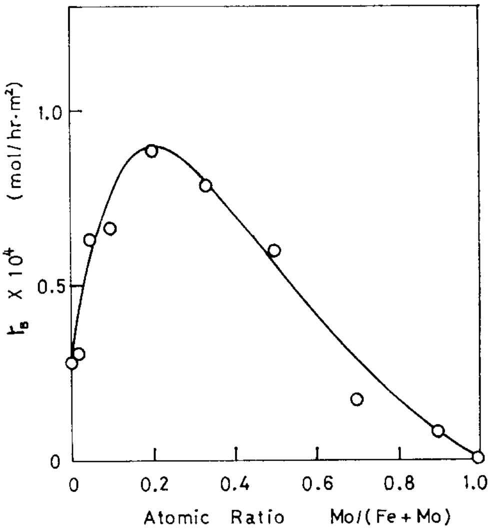

FIG. 8. Oxidation activity for butadiene as a function of the MoO_3 content: $T=320°C$, butadiene $=0.67$ mol% in air.

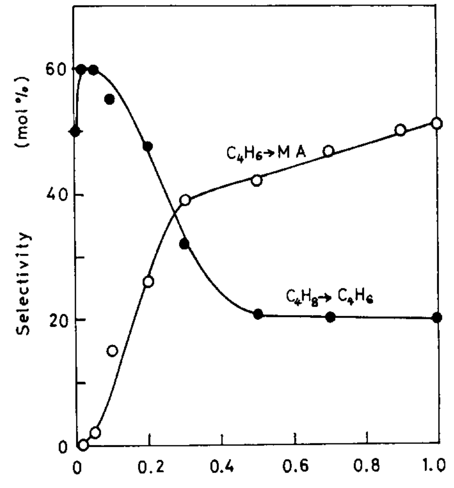

FIG. 9. Selectivity versus the V_2O_5 content: (○) selectivity of butadiene to maleic anhydride, conversion = 40–50%, 0.67 mol% of butadiene in air; (●) selectivity of 1-butene to butadiene, conversion = 30–40%, 1-butene = 0.67 mol%, oxygen = 0.34–1.3 mol% in nitrogen.

acetic acid was fairly small. The selectivity to maleic anhydride at a total conversion of 40–50% is plotted in Figs. 9 and 10. On the other hand, as a model of the Type 2 reactions, the oxidation of 1-butene to butadiene at low oxygen concentration (oxygen = 0.34–1.3 mol% and butene = 0.67 mol%) was chosen. The selectivity at a conversion of 30–40% is also plotted in Figs. 9 and 10.

DISCUSSION

Since the contact oxidation is a reaction between an organic compound and oxygen on the surface of metal oxide, the reaction may be governed by following factors: (1) activation of reactant molecule; (2) reactivity of the activated reactant; (3) activation of oxygen, i.e., incorporation of gaseous oxygen into the crystal lattice oxygen (O^{2-}) by electron transfer from metal oxide to oxygen (*27, 28*); and (4) reactivity of oxygen, i.e., oxidizing power of surface oxygen species.

Factor (2) is dependent largely on the nature of reactant molecule. Thus, the requirements for an oxidation catalyst are functions (1), (3), and (4). Function (3),

$$\underset{\text{(Lewis base)}}{M^{(n-x)+}} + \underset{\text{(Acceptor)}}{O_2} \rightarrow \quad M^{n+} + \underset{\text{(Brønsted base)}}{(x/2)O^{2-}},$$

is dependent both on (a) the electron-donating ability, i.e., the base strength, of the metal ion in a lower oxidation state and (b) the number of active lattice oxygen sites, i.e., the basicity. Function (4) is associated with the strength of the metal–oxygen bonding (M–O). The combination of functions (3) and (4) is defined as the intrinsic oxidation activity. It may be expressed as follows (*19, 20*):

Intrinsic oxidation activity

$$\propto \text{(basicity) } f\text{(M–O and base strength)}$$

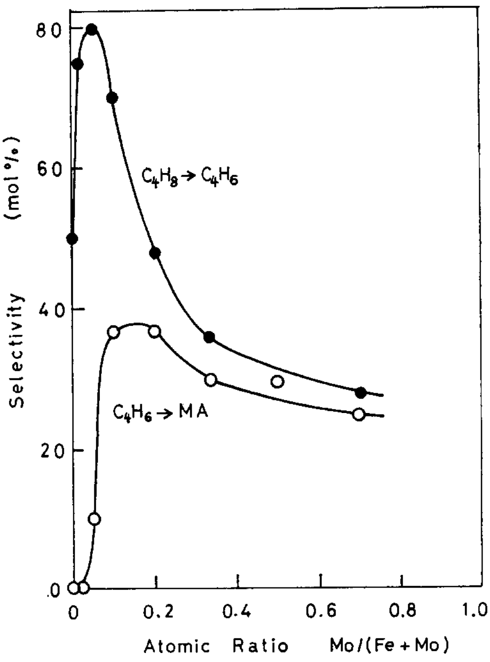

FIG. 10. Selectivity versus the MoO_3 content: (○) selectivity of butadiene to maleic anhydride, conversion = 40–50%, 0.67 mol% of butadiene in air; (●) selectivity of 1-butene to butadiene, conversion = 30–40%, 1-butene = 0.67 mol%, oxygen = 0.34–1.3 mol% in nitrogen.

As has been mentioned above, oxidation activity is governed, more or less, by two functions, that is, activation of the reactant and intrinsic oxidation activity. However, which is the factor deciding the oxidation activity predominantly?

We would like to propose the following hypothesis, as discussed in earlier reports (*19, 25*). When the oxidizing power is weak, the reaction requires a sufficient activation of the reactant molecule. Thus, the oxidation is decided predominantly by the activation of the organic compound rather than by that of oxygen. On the other hand, when the oxidizing power of metal oxide is strong, i.e., when the metal–oxygen bonding strength is weak, the reaction can take place without requiring 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.

Let us now discuss the experimental results from this point of view. The oxidation activity of the Fe_2O_3–MoO_3 system varies in much the same fashion as does the acidity shown in Fig. 3. This finding is in line with the results obtained with the other MoO_3-containing catalysts, and it indicates that the activity is governed mainly by activation of the reactant. On the other hand, the oxidation activity of the Fe_2O_3–V_2O_5 system is fairly high compared with that of the Fe_2O_3–MoO_3 system, and it increases more sharply than the acidity upon the addition of V_2O_5 in the low range of $V < 20$ at%. This implies that activation of the reactant by acidic sites is not the sole factor deciding the oxidation activity.

From the results we are induced to assume the following. Since Fe_2O_3–V_2O_5 has a fairly high oxidizing power, the oxidation activity is affected, to a considerable extent, by the activation of oxygen on basic sites as well as by that of the reactant on acidic sites when the catalyst is rather basic and the activation of olefin by acidic sites is not sufficient, while, when the catalyst is acidic and the activation of reactant becomes sufficient, the contribution of the basic sites decreases.

With regard to the selectivity, a high selectivity to maleic anhydride is obtained with acidic catalysts ($V > 30$ at% and $Mo > 10$ at%). This supports the proposal derived from the earlier studies that a requirement for an effective catalyst for this type of oxidation is possession of acidic properties, because (i) the acidic catalyst is active in the oxidation of such basic reactants as olefin and (ii) it is inactive in the degradation of the acidic product.

The loss in the selectivity upon the addition of MoO_3 of more than about 40 at% may be ascribed to the marked decrease in the oxidation activity. The low selectivity of the Fe_2O_3–MoO_3 system compared with that of the Fe_2O_3–V_2O_5 system may also be ascribed to the evidence that the former is much less active than the latter, because, as the catalyst becomes less active, more severe reaction conditions, which may direct the reaction toward complete combustion, are required to achieve an appreciable conversion.

On the other hand, though the selectivity from butene to butadiene increases upon the addition of a small amount (2–10 at%) of V_2O_5 or MoO_3, it decreases gradually upon the further addition of V_2O_5 or MoO_3. These results can be explained according to the view proposed in earlier works (*20–25*) that a requirement for an effective catalyst in this type of oxidation is a moderate character both in the acid and the base. Fe_2O_3 by itself is too basic to be satisfactory even for this type of oxidation; i.e., its acidic properties are not sufficient to activate the reactant molecule, and so butene, without being activated, is oxidized nonselectively by oxygen species with a relatively high oxidizing power under severe conditions. The acid–base properties proper to this type of reactions can be obtained by the addition of small amounts of such acidic compounds as V_2O_5 and MoO_3. However, when the content of V_2O_5 or MoO_3 exceeds the proper amount, the catalysts become too acidic and the reaction cannot stop at the step of butadiene, because butadiene as well as butene is activated and oxidized on the acidic sites.

It is concluded that, with the change in the composition, the acid-base properties of Fe_2O_3-based oxides vary in a manner similar to those of TiO_2- and SnO_2-based oxides. The catalytic activity and selectivity in the oxidation of olefins can be relatively well understood in terms of their acid–base properties, much as in the case of many other V_2O_5- or MoO_3-containing catalysts.

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