# The Oxidation Activity and Acid-base Properties of Mixed Oxide Catalysts Containing Titania. I. The $TiO_2$-$MoO_3$ and $TiO_2$-$V_2O_5$ Systems

Mamoru Ai

*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152*

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The amounts of both the acidic and basic sites of two series of catalysts, $TiO_2$–$MoO_3$ and $TiO_2$–$V_2O_5$, with different compositions were measured by studying the adsorption of the basic and acidic molecules in the gas phase, using both the static and pulse methods. The acidity of $TiO_2$–$MoO_3$ catalysts is very high at Mo=40—60 atom%, though those of the $TiO_2$-rich (Mo<30 atom%) and $MoO_3$-rich (Mo>80 atom%) catalysts are fairly low. The acidity of the $TiO_2$–$V_2O_5$ increases steadily with the $V_2O_5$ content. The basicity of the catalysts is remarkably enhanced by the introduction of a small amount of $MoO_3$ or $V_2O_5$. It can be said that the catalysts are basic at Mo <20 atom% or V<10 atom%, while the $MoO_3$-rich or $V_2O_5$-rich catalysts are acidic. The vapor-phase oxidation of 1-butene, butadiene,and acetic acid, the dehydration and dehydrogenation of isopropyl alcohol (IRA), and the isomerization of 1-butene were carried out in the presence of an excess of air, and the relationship between the catalytic behavior and the acid-base properties was investigated. It was concluded that the activities and selectivities can be relatively well explained by the acid-base properties between the catalyst and the reactant.

Single $TiO_2$ is impractical as a catalyst because of its low activity. However, mixed-oxide systems combining $TiO_2$ with such oxides as $V_2O_5$, $MoO_3$, $P_2O_5$, $K_2SO_4$, $SiO_2$, and ZnO are known to be effective for certain reactions.[1–5] These combinations seem to induce an unexpectedly great change in the catalytic behavior. Above all, the characteristic features of the selectivity become completely different as different sorts of oxides are introduced into $TiO_2$. However, the function of these second components has not yet been firmly established.

According to our recent studies,[6] it has been found that $TiO_2$, much like $UO_3$, $SnO_2$, and $Fe_2O_3$, is a metal oxide included in Group B, intermediate between such acidic metal-oxides as $V_2O_5$, $MoO_3$, and $WO_3$ (Group A) and such basic metal-oxides with a high oxidation powder as NiO, $Co_2O_3$, $MnO_2$, CuO, and $Cr_2O_3$ (Group C), and that its acid-base properties are significantly modified by the introduction of a small quantity of acidic or basic elements, such as $P_2O_5$, $MoO_3$, and $K_2O$.

It seemed, therefore, that it would be very interesting to find how the incorporation of certain oxides into$TiO_2$ modifies the acid-base properties of the catalyst and how this modification in turn induces a change in the catalytic behavior.

The present paper will deal with the first part of an investigation concerning the oxidation activity of the $TiO_2$-based catalyst systems. We attempted to ascertain how the incorporation of various amounts of $MoO_3$ and $V_2O_5$ into $TiO_2$ modified the acid-base properties as well as the oxidation activity and selectivity, and examined to see whether or not the catalytic behavior can be explained by the acid-base properties of the catalyst system, as in the cases of the $V_2O_5$–$MoO_3$,[7] $V_2O_5$–$P_2O_5$,[8] $MoO_3$–$P_2O_5$,[9] $MoO_3$–$Bi_2O_3$–$P_2O_5$,[10–12] $MoO_3$–$P_2O_5$–$X_nO_m$[13] $SnO_2$–$V_2O_5$,[14,15] and $SnO_2$–$MoO_3$[14,16] systems.

## Experimental

*Catalysts.* Two series of $TiO_2$-based binary catalysts, $TiO_2$–$MoO_3$ and $TiO_2$–$V_2O_5$, with different compositions were prepared as follows. The required quantity of $TiCl_4$ was dissolved in water containing ice. To this solution, dilute aqueous ammonia was added to precipitate the hydroxide. After filtering and washing, the paste-like hydroxide was added to an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ or $NH_4VO_3$–oxalic acid, and 10—20 mesh pumice was mixed with the solution; then the mixture was evaporated with vigorous stirring. The amount of pumice was 500 ml (about 150 g) per g atom of titanium and molybdenum or titanium and vanadium. The catalyst was calcined under flowing air at 500 °C for about 4—5 h.

*Acidity and Basicity Measurements.* Since the $TiO_2$–$MoO_3$ and $TiO_2$–$V_2O_5$ catalysts are colored and small in surface area, the determination of the acidity and basicity by an ordinary titration method seems to be difficult; therefore, the adsorption amounts of the basic and acidic molecules in the gas phase were measured, much as in a previous work.[12]

*(a) 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 small areas. 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 h under a stream of dried air. Immediately after the vessel had then been taken out of the furnace, it was quickly connected to the adsorption apparatus and pumped out. A known amount of $NH_3$ or $CO_2$ was introduced into the adsorption system, after which it was allowed to stand for 20 min before the pressure changes were read. Subsequently, the catalyst was pumped out for 30 min at the same temperature. Similar adsorption procedures were then repeated, and the amount of 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; this was adopted as a measure of the acidity or basicity of the catalysts.

*(b) Gas-chromatographic Pulse Technique*: The apparatus used was a conventional gas chromatograph equipped with a U-tube of stainless steel (4 mm in internal diameter and 40 cm in length). The catalyst (1.0 g) was packed in the U-tube and heat-treated in a stream of air at 500 °C for 1 h. Immediately after the U-tube had then been taken out from the furnace, it was quickly connected to the gas chromatographic column, unless otherwise indicated, and placed in another

furnace kept at 130 °C or 160 °C. Then the carrier gas (He: 50 ml NTP/min) was introduced into the system.

In the case of the basicity measurements acetic acid was chosen as the acidic adsorbate, much as in previous works.[12,15,16]) A sequence of the pulses of an heptane solution of 1.0 M acetic acid was injected into the U-tube (130 °C) at intervals of about 2 min. The volume of the pulses was 3—10 μl, 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 at both the inlet and the exit of the U-tube. The peak of acetic acid at the exit is not observed upon the initial injections; as the number of pulse increases, the catalyst is saturated with the acetic acid, 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 basicity.

In the case of the acidity measurements, butene pulses consisting of 2 ml of a mixture of air and 1-butene (0.7 mol%) and pyridine pulses consisting of 2—5 μl of an hexane solution of 0.25 M pyridine were fed into the U-tube (160 °C) alternately and separately; the amount of pyridine required to inhibit the isomerization of 1-butene completely was adopted as a measure of the acidity.

*Catalytic-activity Measurements.* The vapor-phase oxidation of 1-butene, 1,3-butadiene, and acetic acid, the isomerization of 1-butene, and the dehydration and dehydrogenation of isopropyl alcohol (IPA) were carried out in an ordinary continuous-flow-type reaction system. The concentrations of butene, butadiene, acetic acid, and IPA were about 0.67, 0.67, 1.5, and 1.65 mol% respectively in air, unless otherwise indicated. The total flow rate (at 25 °C) was kept constant at 1.5 l/min, and the amount of the catalyst used was 1.0—25 g. The reactor and the experimental and analytical procedures were the same as those employed in previous works.[6–16])

## Results

*Surface Areas.* The surface areas of the $TiO_2$–$MoO_3$ and $TiO_2$–$V_2O_5$ catalysts were checked by the BET method using nitrogen at −195 °C. The results are shown in Table 1. The surface area increases sharply upon the addition of even 2 atom% of $MoO_3$ to $TiO_2$, but with a further increase in the $MoO_3$ content it gradually decreases.

TABLE 1. SURFACE AREA OF THE $TiO_2$–$MoO_3$ AND $TiO_2$–$V_2O_5$ CATALYSTS USED

| Composition Mo/(Ti+Mo) | Surface area ($m^2/g$) | Composition V/(Ti+V) | Surface area ($m^2/g$) |
|---|---|---|---|
| 0 | 2.0 | 0 | 2.0 |
| 0.02 | 45.2 | 0.02 | 4.3 |
| 0.05 | 38.8 | 0.05 | 5.7 |
| 0.10 | 38.5 | 0.10 | 8.0 |
| 0.20 | 39.2 | 0.20 | 4.2 |
| 0.33 | 27.4 | 0.33 | 4.0 |
| 0.50 | 13.3 | 0.50 | 4.1 |
| 0.70 | 14.9 | 0.70 | 4.0 |
| 0.80 | 10.0 | 0.90 | 4.8 |
| 0.90 | 8.5 | 1.0 | 2.8 |
| 0.95 | 7.5 | | |
| 1.0 | 2.6 | | |

*Acidity.* Since even single $TiO_2$ has a fair amount of acidic sites,[4,17,18]) probably of a very weak acid strength compared with the $MoO_3$-rich or $V_2O_5$-rich catalysts, $NH_3$ was adsorbed even on the pure $TiO_2$ and on the $TiO_2$-rich catalysts to almost the same extent as on the $MoO_3$-rich or $V_2O_5$-rich catalysts at room temperature. However, at a higher temperature (more than 350 °C), the decomposition of $NH_3$ was enhanced and adsorption measurement became impossible.

In the case of adsorption measurements by the pulse method, the $TiO_2$-rich catalysts adsorbed pyridine at 130 °C to the same extent as the $MoO_3$-rich or $V_2O_5$-rich catalysts. This means that the pure $TiO_2$ has a fair amount of certain acidic sites and that this method is not proper.

Therefore, as a measure of the acidity, the amount of pyridine required to poison the isomerization of butene completely was adopted.[15,16,19]) However, the defect of this method is that the isomerization must be catalyzed mainly by acidic sites; when the isomerization is catalyzed by other factors, *i.e.*, when the catalyst is basic rather than acidic, this method cannot be used. To remove this defect, prior to the adsorption measurements the heat-treated catalysts were placed under a stream of a mixed gas of air and 1-butene (0.67 mol%) at 250 °C for 30 min; this was done because of the experimental evidence that, under the circumstances of the oxidation of butene, the isomerization of butene is uniquely dependent on the acidic sites of the catalyst (as will be described below).

The acidity per unit of the surface area of the $TiO_2$–$MoO_3$ and $TiO_2$–$V_2O_5$ catalysts, as determined both by the amount of $NH_3$ irreversibly adsorbed at 200 °C and 250 °C and by that of pyridine required to poison completely the isomerization activity for 1-butene at 160 °C, is plotted as a function of the $MoO_3$ or $V_2O_5$ content in Figs. 1 and 2.

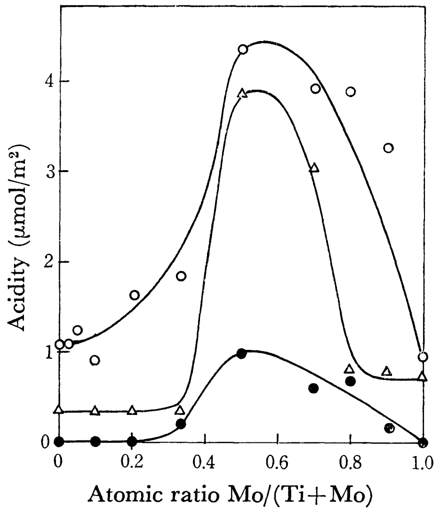

Fig. 1. Acidity of $TiO_2$–$MoO_3$ as a function of the $MoO_3$ content. Irreversible adsorption of $NH_3$ (static method) at 200 °C: ○, at 250 °C: △, pyridine required to poison the isomerization activity for 1-butene at 160 °C (pulse method): ●.

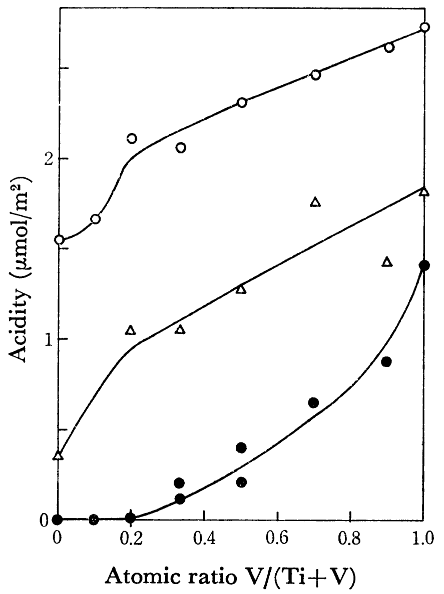

Fig. 2. Acidity of $TiO_2$–$V_2O_5$ as a function of the $V_2O_5$ content. Irreversible adsorption of $NH_3$ (static method) at 200 °C: ○, at 250 °C: △, pyridine required to poison the isomerization activity for 1-burene at 160 °C (pulse method): ●.

Parallels were found between the amounts of $NH_3$ obtained by means of the static method and those of pyridine obtained by means of the pulse method; these parallels may indicate the validity of these results, though the value of $NH_3$ was much higher than that of pyridine. It is believed that, even at 250 °C, $NH_3$ is still adsorbed on the acidic sites of a weak acid strength, which cannot serve to catalyze the isomerization.

The results show that the acidity is fairly low in the low range of the $MoO_3$ content (Mo<30 atom%), but that it increases rapidly with the $MoO_3$ content, shows a maximum at about Mo=40—60 atom%, and then decreases again to a very low value of pure $MoO_3$. It is also found that, in the case of the $TiO_2$–$V_2O_5$ catalysts, the acidity increases steadily with the $V_2O_5$ content.

*Basicity.* The basicity per unit of surface area of the $TiO_2$–$MoO_3$ and $TiO_2$–$V_2O_5$ catalysts, as determined by the irreversible adsorption of acidic molecules in the gas phase, is shown in Figs. 3 and 4 as a function of the $MoO_3$ and $V_2O_5$ content. Parallels were found between the amounts of $CO_2$ obtained by means of the static method and those of acetic acid obtained by means of the pulse method. The difference may be attributed to the difference in acid strength between $CO_2$ and acetic acid, and the acetic acid may be adsorbed on the basic sites of a lower base strength than $CO_2$.

It is evident at least that, with an increase in the $MoO_3$ and $V_2O_5$ content, the basicity sharply increases at first, passes through a maximum at about Mo=5 atom% or V=5 atom%, and then decreases of the very low value of the pure $MoO_3$ or $V_2O_5$ catalyst.

*Dehydration and Dehydrogenation Activities for IPA.* Because of the difficulty implicit in the titration method, we used, in our previous studies,[6–11,13,14] the catalytic activity for the dehydration of IPA to propylene as a measure of the acidity of the catalyst, and the (dehydrogenation rate)/(dehydration rate) ratio in the reaction of IPA as a measure of the basicity, assuming that the dehydration is catalyzed at acidic sites and that the dehydrogenation is catalyzed at both acidic and basic sites. It is, therefore, very interesting and important to confirm whether or not these measures of acidity and basicity obtained from the catalytic activities for IPA really represent their true values.

A gaseous mixture of IPA and air was passed through a bed of the catalyst held at a temperature of 165—185 °C. The amount of the catalyst was changed in the 3—30 g range. Apart from propylene and acetone, only di-isopropyl ether was found in the product, but the

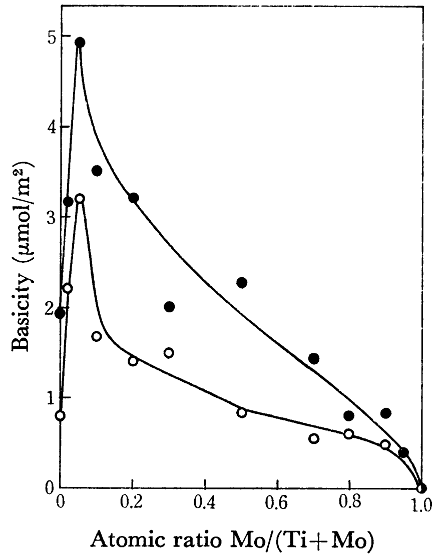

Fig. 3. Basicity of $TiO_2$–$MoO_3$ as a function of the $MoO_3$ content. Irreversible adsorption of $CO_2$ at 20 °C (static method): ○, acetic acid at 130 °C (pulse method): ●.

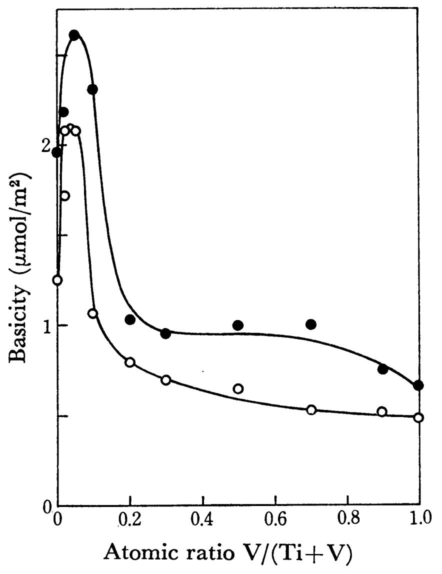

Fig. 4. Basicity of $TiO_2$–$V_2O_5$ as a function of the $V_2O_5$ content. Irreversible adsorption of $CO_2$ at 20 °C (static method): ○, irreversible adsorption of acetic acid at 130 °C (pulse method): ●.

amount of this ether was very small compared with the amount of the other two compounds. The initial rates of the dehydration and dehydrogenation at 175 °C, $r_p$ and $r_a$ (mol/h m²-cat), were measured; they are plotted, together with the $r_p/r_a$ ratio, in Figs. 5 and 6.

At Mo<20 atom% or V<20 atom%, the dehydrogenation takes place rather than the dehydration, but at Mo>40 atom% or V>60 atom% the dehydration is predominant. As the content of $MoO_3$ or $V_2O_5$ increases, the values of $r_p$ and $r_a/r_p$ vary in the same direction as the acidity and basicity (Figs. 1—4).

*Isomerization Activity for Butene.* The isomerization of butene is sometimes accompanied by its oxidation. The relationship between the catalytic activity for the isomerization and the acid-base properties was investigated. The reaction was carried out at 0.67 mol% of 1-butene in air and at 225 °C by changing the catalyst amount in the 1—20 g range. As a measure of the isomerization activity, we adopted, for convenience, the ratio of (*cis*-2-$C_4H_8$+*trans*-2-$C_4H_8$)/(1-$C_4H_8$+*cis*-2-$C_4H_8$+*trans*-2-$C_4H_8$) corresponding to 1 m² of the catalyst, *I*.

The results are plotted as a function of the catalyst composition in Figs. 7 and 8. It is found that the isomerization activity changes in a manner similar to the acidity shown in Figs. 1 and 2.

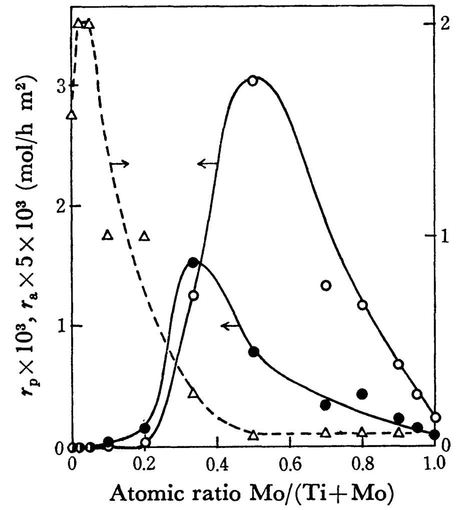

Fig. 5. The dehydration and dehydrogenation activities for IPA, $r_p$ and $r_a$, and the $r_a/r_p$ ratio as a function of the $MoO_3$ content.
Catalyst=$TiO_2$-$MoO_3$, $T$=175 °C, IRA=1.65 mol% in air, Dehydration: ○, Dehydrogenation: ●. $r_a/r_p$: △.

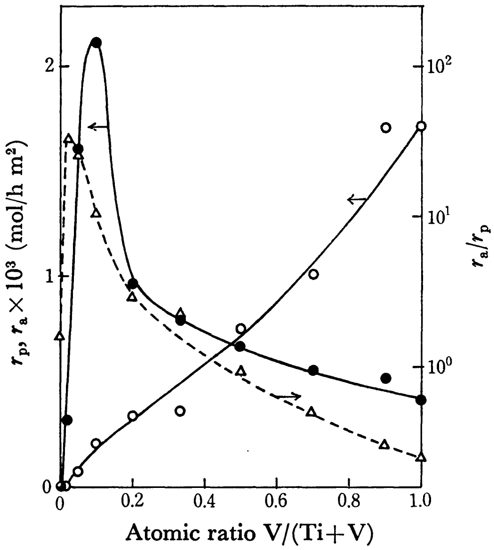

Fig. 6. The dehydration and dehydrogenation activities for IPA, $r_p$ and $r_a$, and the $r_a/r_p$ ratio as a function of the $V_2O_5$ content.
Catalyst=$TiO_2$-$V_2O_5$, $T$=175 °C, IPA=1.65 mol% in air, Dehydration; ○, Dehydrogenation: ●, $r_a/r_p$: △.

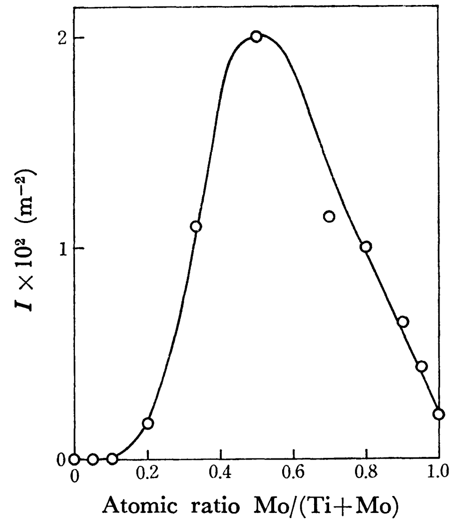

Fig. 7. The isomerization activity for 1-butene as a function of the $MoO_3$ content. Flow rate=1.5 l/min, 1-$C_4H_8$=0.67 mol% in air, $T$=225 °C, $I$=ratio of (*cis*-2-$C_4H_8$+*trans*-2-$C_4H_8$)/(1-$C_4H_8$+*cis*-2-$C_4H_8$+*trans*-$C_4H_8$) corresponding to 1 m² of the catalyst.

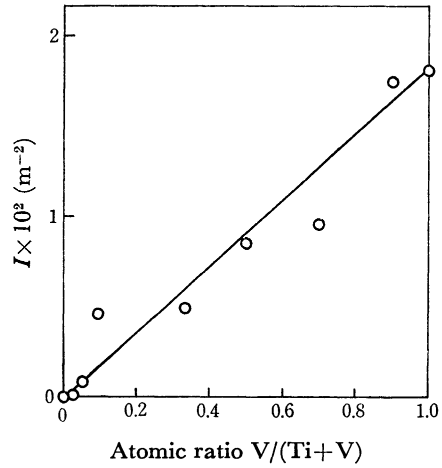

Fig. 8. The isomerization activity for 1-butene as a function of the $V_2O_5$ content. Total flow rate=1.5 l/min, 1-$C_4H_8$=0.67 mol% in air, $T$=225 °C,

*Oxidation Activity for Butadiene.* First, in order to examine the oxidation activity for basic reactants, butadiene was oxidized in an excess of air. The initial rate of the overall consumption of butadiene, at 320 °C in the case of the $TiO_2$–$MoO_3$ catalysts and at 290 °C in the case of the $TiO_2$–$V_2O_5$, $r_B$ (mol/h $m^2$-cat), was adopted, for convenience in the experimental procedures, as a measure of the oxidation activity. It is plotted as a function of the catalyst composition in Figs. 9 and 10.

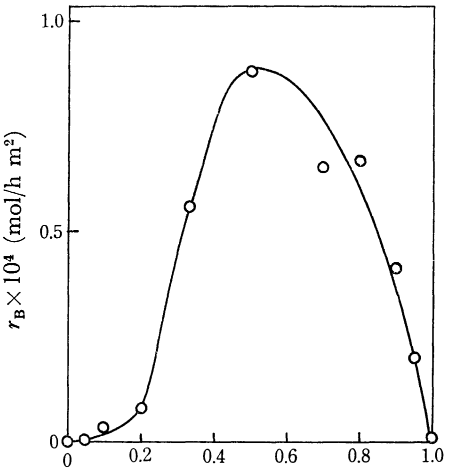

Fig. 9. The oxidation activity for butadiene as a function of the $MoO_3$ content. Catalyst=$TiO_2$–$MoO_3$, Butadiene=0.67 mol% in air, $T$=320 °C,

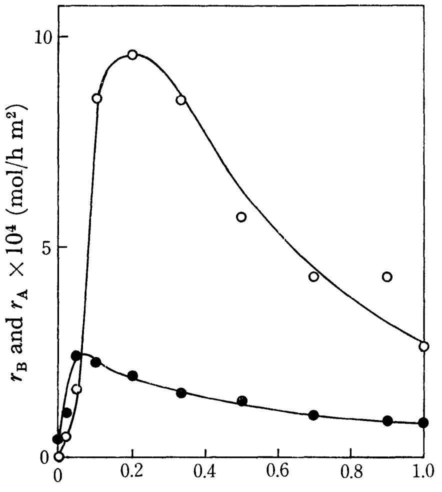

Fig. 10. The oxidation activities for butadiene and acetic acid as a function of the $V_2O_5$ content. Catalyst=$TiO_2$–$V_2O_5$,
○: butadiene, $C_4H_6$=0.67 mol% in air, $T$=290 °C,
●: acetic acid, $C_2H_4O_2$=1.5 mol% in air, $T$=290 °C.

The oxidation activity of $TiO_2$–$MoO_3$ catalysts increases with the $MoO_3$ content and attains a maximum at about Mo=50 atom%. The trend of the $r_B$ curve is in agreement with that of the acidity shown in Fig. 1. On the other hand, in the case of $TiO_2$–$V_2O_5$ catalysts, the $r_B$ increases sharply with the addition of even a small amount of $V_2O_5$ and attains a maximum at V=20 atom%. The trend of the $r_B$ curve is quite different from that of the acidity shown in Fig. 2.

*Oxidation Activity for Acetic Acid.* Next, the oxidation activity for acidic compounds was examined in the case of $TiO_2$–$V_2O_5$ catalsts. Acetic acid was chosen as the acidic reactant, and the initial rate of the oxidation to $CO_2$ at 290 °C in the presence of an excess of air, $r_A$ (mol/h $m^2$-cat), was taken as the oxidation activity. The results are shown in Fig. 10. The $r_A$ increases with an increase in the $V_2O_5$ content and passes through a maximum at about V=10 atom%.

*Selectivity in the Oxidation of Olefin.* The starting materials in selective oxidations are mostly such basic compounds as olefinic and aromatic hydrocarbons. The reactions, therefore, can be divided into two types in terms of the acid-base characteristics of the products:[6,10–12,14–16)]

Type 1: Basic reactant ⟶ acidic product
Type 2: Basic reactant ⟶ basic product

As a model reaction of Type 1, the oxidation of butadiene to maleic anhydride in the presence of an excess of air (0.67 mol% $C_4H_8$) was chosen. The

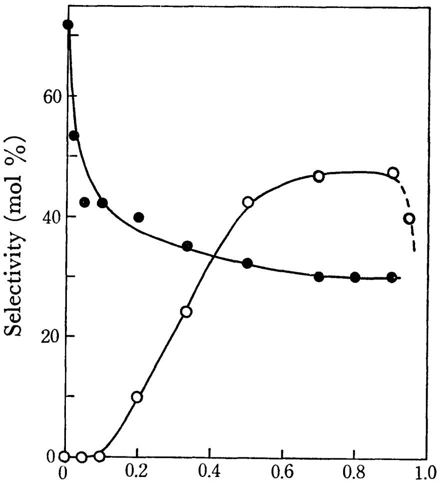

Fig. 11. Selectivity *versus* the $MoO_3$ content.
○: selectivity of butadiene to maleic anhydride,
●: selectivity of 1-butene to butadiene.

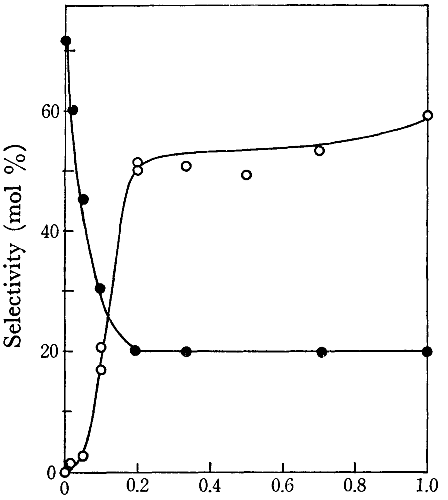

Fig. 12. Selectivity *versus* the $V_2O_5$ content.
○: selectivity of butadiene to maleic anhydride,
●: selectivity of 1-butene to butadiene.

selectivity at a conversion of about 40—50% was measured for every catalyst; it is plotted as a function of the catalyst composition in Figs. 11 and 12.

On the other hand, as a model of the Type 2 reactions, the oxidation of 1-butene to butadiene at a low oxygen concentration ($O_2$=0.34—1.3 mol% and $C_4H_8$=0.67 mol%) was chosen. The selectivity at a conversion of about 30—40% was measured; it is also plotted in Figs. 11 and 12.

A high selectivity to maleic anhydride is obtained over the acidic catalysts (Mo>50 atom% and V>20 atom%), while the selectivity to butadiene decreases steadily with the $MoO_3$ and $V_2O_5$ content.

## Discussion

These experiments first show that the incorporation of $MoO_3$ and $V_2O_5$ induces a change in the surface area; this change directly contributes to the catalytic activity.

Next, the incorporation of $MoO_3$ and $V_2O_5$ modifies, to a significant extent, the acid-base properties of the catalyst systems. In a $MoO_3$-poor (Mo<20 atom%) or $V_2O_5$-poor (V<10 atom%) composition, the catalysts are basic; the catalysts containing more than 40 atom% Mo or 20 atom% V are acidic. It should be noted that, although $MoO_3$ and $V_2O_5$ are typical acidic elements, the incorporation of a minor amount of $MoO_3$ (Mo=2—10 atom%) or $V_2O_5$ (V=2—10 atom%) into $TiO_2$ remarkably enhances the basicity, much as in the cases where $MoO_3$ and $V_2O_5$ were combined with $SnO_2$ and $Fe_2O_3$.14–16,20) This phenomenon resembles the fact that the incorporation of a minor amount of $Bi_2O_3$, which is a basic element, into $MoO_3$–$P_2O_5$ enhances the acidity.10–12) The acidity per unit of the surface area of the $TiO_2$–$MoO_3$ system attains a sharp maximum at about 50 atom% Mo, much as in the case of the $SnO_2$–$MoO_3$ system. However, the acidity of the $TiO_2$–$MoO_3$ system at Mo=50 atom% is considerably lower than that of the $SnO_2$–$MoO_3$ at Mo=50 atom-%.14,16,20) The incorporation of $V_2O_5$ to $TiO_2$ never enhance the acidity per unit of the surface area more than $V_2O_5$ itself, unlike the case of the $TiO_2$–$MoO_3$ and $MoO_3$–$V_2O_5$ systems.7)

A comparison of the catalytic activities for IPA with the acidity-basicity data reveals that the activity for the dehydration to propylene, $r_p$, respresents the acidity of the catalyst, and that the value of the $r_a/r_p$ ratio is also valid enough as a rough index of the basicity, much as in the cases of the $MoO_3$–$Bi_2O_3$–$P_2O_5$,12) $SnO_2$–$V_2O_5$,15) and $SnO_2$–$MoO_3$ systems.16) Therefore, this indirect method of acidity-basicity measurement, based on the catalytic activity, may be recommended especially in the cases of catalysts whose surface area are too small for the amount of adsorption to be measured.

The isomerization activity for butene is correlated only with the acidity, not with the basicity, and the product ratio of *cis-/trans*-2-butene is 1—2. These pieces of evidence prove that, under the circumstances of the oxidation, the isomerization is catalyzed only by the acidic sites.4,17,18) The same results have been observed in all the catalyst systems examined by us, such as $V_2O_5$–$MoO_3$, $V_2O_5$–$P_2O_5$, $MoO_3$–$P_2O_5$, $MoO_3$–$Bi_2O_3$–$P_2O_5$, $MoO_3$–$P_2O_5$–$X_nO_m$, $SnO_2$–$V_2O_5$, and $SnO_2$–$MoO_3$.6–16) This means that the basic sites which can also catalyze the isomerization in the absence of oxygen in a closed or a pulse-reaction system are poisoned by $CO_2$, $H_2O$, or other acidic oxidation-products under the circumstances o the oxidation.

The similarity of the $r_B$ curve in Fig. 9 to the acidity curves in Fig. 1 suggests that, in the case of $TiO_2$–$MoO_3$ catalysts, the acidic sites play an important role in the oxidation of olefin, probably in the activation of the olefin, much as in the cases of the $V_2O_5$–$MoO_3$, $V_2O_5$–$P_2O_5$, $MoO_3$–$P_2O_5$, $MoO_3$–$Bi_2O_3$–$P_2O_5$, $MoO_3$–$P_2O_5$–$X_nO_m$, and $SnO_2$–$MoO_3$7–14,16) systems.

On the other hand, in the case of the $TiO_2$–$V_2O_5$ system, the shapes of the $r_B$ curves (Fig. 10) are completely different from those of the acidity curves in Fig. 2. This implies that acidic sites are not the sole factor deciding the oxidation activity for butadiene. To explain these results, we envisage that, when the catalyst is highly acidic and scarcely basic, as in the cases of the $V_2O_5$–$MoO_3$,7) $V_2O_5$–$P_2O_5$,8) and $MoO_3$–$P_2O_5$ systems,9) the oxidation activity for such a basic reactant as olefin is controlled only by the activation of olefin, which is performed at the acidic sites of the catalyst. However, as the acidic property of the metal-oxide catalst decreases and as the basic property increases, the contribution of the acidic sites to the oxidation activity decreases, while that of the activation of oxygen, which is connected, presumably, with the number of basic sites, *i.e.*, $O^{2-}$ sites, on the surface of the catalyst as well as with oxygen-mobility of the sites increases.12,20) Practically, in the case of oxidation over such scarcely acidic catalysts as the Ni, Co, Cr, Mn, and Cu metal oxides, the oxidation activity must be controlled entirely by the activity of surface oxygen—that is, by the oxidizing power of surface oxygen.6,21)

Therefore, it may be speculated that, in the case of the $TiO_2$–$V_2O_5$ system, both the acidic and basic sites participate in the oxidation to a certain extent; when the $V_2O_5$ content is low and the catalyst is rather basic, the oxidation is affected to a considerable extent by the activity of the surface oxygen, while, as the $V_2O_5$ content increases, the contribution of the acidic sites increases, and when the $V_2O_5$ content is high and the catalyst becomes highly acidic, the contribution of the acidic sites becomes predominant. The fact that the oxidation activity of the $TiO_2$–$MoO_3$ system is much lower than that of the $TiO_2$–$V_2O_5$ system, though the former has a much higher acidity than the latter, may also support the theory of the participation of the factor relating to the activation of surface oxygen.

The characteristics of the $r_A$ curve in Fig. 10 are similar to those of the $r_a$ curves in Fig. 6. This may suggest that basic sites play a fairly important role in the oxidation, probably in the activation of the acidic compound.6,12,20)

It is evident at least that, when the $V_2O_5$ content is low (V<5 atom%) where the $TiO_2$–$V_2O_5$ catalyst is basic, the catalyst is less active for the oxidation of a base reactant such as butadiene than for the oxidation of an acidic reactant such as acetic acid, while when the catalyst is rich in $V_2O_5$ content and highly acidic, the catalyst is more active for butadiene than for an acidic compound.

With regard to the selectivity, the characters of the maleic anhydride curves in Figs. 11 and 12 support our opinion[6–16] that one requirement for an effective catalyst in this type of reaction (acid-formation reaction) is the acidic property; this may be concluded for two reasons: (1) the acidic catalyst is active in the oxidation of the reactant, and (2) it is inactive in the degradation of the acidic compound produced. On the other hand, the character of the curve of the butadiene formation may reveal that $TiO_2$ itself has both the acidic and basic properties proper to the selectivity of this type of reaction (base-formation reaction) and that the increase in the acidic character as a result of the $MoO_3$ or the $V_2O_5$ addition leads to a decrease in the selectivity. It should be noted that, in the cases of $SnO_2$ and $Fe_2O_3$, which are less acidic and more basic than $TiO_2$,[14,16,20] the selectivity increases with the addition of a small amount of such acidic elements as $MoO_3$ and $V_2O_5$. It seems probable that the presence of the acidic character is desirable in enhancing the activity for the reactant; however, when the acidic character is too high, butadiene is oxidized more rapidly than butene,[10–12] because butadiene is more basic that butene (the ionization potential of butadiene 8.75—9.18 eV, is lower than that of butene, 9.3—9.8 eV). These results also support our opinion[6–16] that one requirement for an effective catalyst in a base-formation reaction is a moderate character both in an acid and a base.

It can be concluded that the oxidation activity and selectivity of the $TiO_2$–$MoO_3$ and $TiO_2$–$V_2O_5$ catalysts can be relatively well interpreted in connection with their acid-base properties, which are strongly changed by the catalyst composition.

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