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The Oxidation Activity and Acid-Base Properties of SnO_2-Based Binary Catalysts

I. The SnO_2-V_2O_5 System

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The amounts of both the acidic and basic sites of a series of SnO_2-V_2O_5 catalysts 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 acidities of the catalysts are fairly low in the low range of V_2O_5 content ($V < 20$ atom%); the acidity per unit of weight shows a maximum at about $V = 40$-50 atom%, but the acidity per unit of surface area increases continuously with the V_2O_5 content. On the other hand, the pure SnO_2 has a fair basicity, and the introduction of a smal amount of V_2O_5 ($V = 2$-20 atom%) to SnO_2 remarkably enhances the basicity. It can be said that the SnO_2-rich ($V < 20$ atom%) catalysts are basic, while the V_2O_5-rich catalysts are acidic. The vapor-phase oxidation of 1-butene and butadiene, the isomerization of 1-butene, and the dehydration and dehydrogenation of isopropyl alcohol (IPA) 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.

INTRODUCTION

Single SnO_2 is impractical as an oxidation catalyst because of its low activity. However, the mixed oxide systems combining SnO_2 with some other metal oxides are known to be very effective for certain selective oxidations (*1*). There have already been several scientific reports on partial oxidations using such SnO_2-containing binary catalysts as SnO_2-V_2O_5 (*2*), SnO_2-MoO_3 (*3*), SnO_2-P_2O_5 (*4*), SnO_2-Sb_2O_5 (*5*), and SnO_2-Bi_2O_3 (*6,7*). 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 metal oxides are incorporated into SnO_2. However, the function of the second components has not yet been firmly established.

According to our recent studies (*8*) it has been found that SnO_2, much like UO_3, TiO_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 oxide with a high oxidation power 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 acidic metal oxides into SnO_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 deals with the first part of an investigation concerning the oxidation activity of the SnO_2-based binary catalyst systems. We attempted to ascertain how the incorporation of various amounts of V_2O_5 into SnO_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 system, as in the cases of the V_2O_5–MoO_3 (*9*), MoO_3–Bi_2O_3–P_2O_5 (*10–12*), MoO_3–P_2O_5 (*13*), MoO_3–P_2O_5–X_nO_m (*14*), and V_2O_5–P_2O_5 (*15*) systems.

EXPERIMENTAL METHODS

1. Catalysts

A series of binary catalysts of SnO_2–V_2O_5, with 11 different V/Sn ratios (pure SnO_2 and V_2O_5 included) were prepared as follows. The required quantity of NH_4VO_3 was dissolved in hot water by using oxalic acid. To a solution of $SnCl_2 \cdot 2H_2O$, dilute aqueous ammonia was added to precipitate the hydroxide. After filtering and washing, a paste-like hydroxide was added to the NH_4VO_3 solution and 10–20 mesh pumice was mixed into the solution; then the mixture was evaporated with vigorous stirring. The amount of pumice was 500 ml (about 150 g)/g atom of tin and vanadium. The catalyst was calcined under flowing air at 500°C for about 4–5 hr.

2. Acidity and Basicity Measurements

Since the SnO_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, we attempted to measure the acidity and basicity by means of the adsorption of the basic and acidic molecules, respectively, in the gas phase, 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 low 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 hr under a stream of dried air. Immediately after the vessel had 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 vessel, 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 (40 cm in length and 4 mm i.d.). The catalyst (1.0 g) was packed in the U-tube and heat treated in a stream of air at 500°C for 1 hr. Immediately after the U-tube had 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 or 160°C. Then the carrier gas (He: 50 ml NTP/min) was introduced into the system.

Acetic acid was chosen as the acidic adsorbate (*12*). A sequence of the pulses of an *n*-heptane solution of 1.0 *M* acetic acid was injected into the U-tube (130°C) (the pulses were 3–10 μl in size), and the amount of acetic acid required to saturate the catalyst was 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 (*12*).

In the case of acidity measurements, butene pulses consisting of 2 ml of a mixture of air and 1-C_4H_8 (0.7 mol%) and pyridine pulses consisting of 2–5 μl of an *n*-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 completely the isomerization of 1-butene was adopted as a measure of the acidity.

3. *Catalytic-Activity Measurements*

The vapor-phase oxidation of 1-butene and 1,3-butadiene 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, and IPA were about 0.67, and 1.65 mol% in air, respectively, unless otherwise indicated. The total flow rate (at 25°C) was kept constant at 1.5 liters/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 (*8–15*).

RESULTS

1. *Surface Areas*

The surface areas of the SnO_2–V_2O_5 catalysts were checked by the BET method using nitrogen at −195°C. Figure 1 shows the dependency of the surface area on the catalyst composition. It is found that the surface area increases sharply upon the addition of even a small amount (2–5 atom%) of V_2O_5 to SnO_2, and that it passes through a maximum at about 30 atom% V and then decreases again. For example, the SnO_2–V_2O_5 (V = 30 atom%) catalyst has 5–6 times as much surface area as a single SnO_2 or V_2O_5 catalyst.

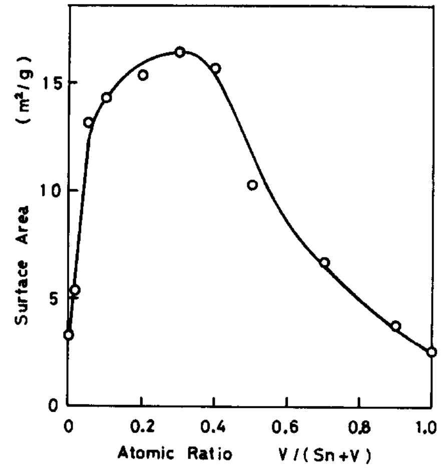

FIG. 1. Effect of the V_2O_5 content on the surface area.

2. *Acidity*

Since even pure SnO_2 has a fair amount of acidic sites (*16*), probably of very weak acid strength compared with the V_2O_5-rich catalysts, NH_3 was adsorbed on the pure SnO_2 and SnO_2-rich catalysts to almost the same extent as on the V_2O_5-rich catalysts at room temperature. However, at a higher temperature (more than 250°C), the decomposition of NH_3 was enhanced.

In the case of the adsorption measurements by the pulse method (*12*), the SnO_2-rich catalysts adsorbed pyridine at 130°C to the same extent as the V_2O_5-rich catalysts. Therefore, we tried to use, as a measure of the acidity, the amount of pyridine required to poison completely the isomerization of butene. 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 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 described below).

The acidity per unit of the surface area of the SnO_2-V_2O_5 catalysts, as determined both by the amount of NH_3 irreversibly adsorbed at 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 V_2O_5 content in Fig. 2.

A parallelism was 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; this parallelism may indicate the validity of those results, though the value of NH_3 was a little 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 reveal that, though the acidity per unit of weight of the SnO_2-V_2O_5 catalysts attains a maximum at about 40–50 atom% V, the acidity per unit the curve becomes gentle with a further increase in the V_2O_5 content.

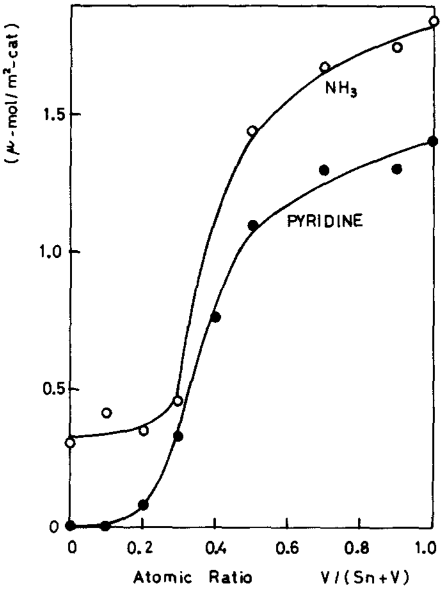

FIG. 2. Acidity of SnO_2-V_2O_5 as a function of the V_2O_5 content: (○) NH_3 at 250°C (static method); (●) pyridine required to poison the isomerization activity for 1-butene at 160°C (pulse method).

3. Basicity

The basicity per unit of surface area of the SnO_2-V_2O_5 catalysts, as determined by the irreversible adsorption of the acidic molecules in the gas phase, is shown in Fig. 3 as a function of the V_2O_5 content. The amount of CO_2 obtained by means of the static method and that of acetic acid obtained by means of the pulse method change in the same direction with an increase in the V_2O_5 content. The difference may be attributed mainly to the difference in the 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 V_2O_5 content, the basicity sharply increases at first, passes through a maximum at about V = 5 atom%, and then decreases to the very low value of the pure V_2O_5 catalyst.

4. Dehydration and Dehydrogenation Activities for IPA

Because of the difficulty in the titration method, 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 (*8–11,13–15*) and the (dehydrogenation rate)/(dehydration rate) ratio in the reaction of IPA as a measure of the basicity (*8,11,15*), 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

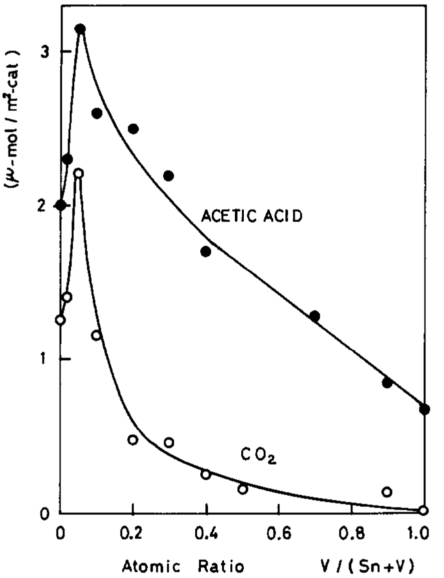

FIG. 3. Basicity of SnO_2–V_2O_5 as a function of the V_2O_5 content: (○) CO_2 at 20°C (static method); (●) acetic acid at 130°C (pulse method).

of the surface area increases continuously with an increase in the V_2O_5 content; this acidity is fairly low in the low range of the V_2O_5, but it rapidly increases with the V_2O_5 content at $V = 20$–50 atom%, and

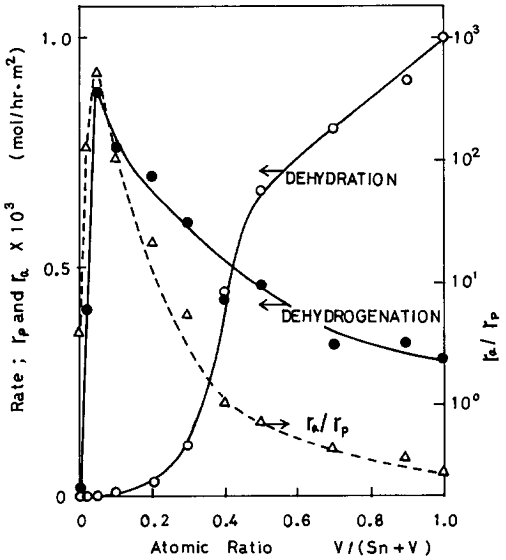

FIG. 4. The dehydration and dehydrogenation activities for IPA, r_p and r_a, and the r_a/r_p ratio, versus the V_2O_5 content: $T = 175°C$, $IPA = 1.65$ mol% in air.

3–30 g range. Apart from propylene and acetone, only diisopropyl ether was found in the product, but the amount of this ether was very small compared with those of the two other compounds. The initial rates of the dehydration and the dehydrogenation at 175°C, r_p and r_a (mol/hr·m²-cat), were measured; they are plotted, together with the r_a/r_p ratio, in Fig. 4.

At $V < 30$ atom% the dehydrogenation takes place rather than the dehydration, but at $V > 40$ atom% the dehydration is predominant. The r_a/r_P ratio increases sharply, passes through a maximum at 5 atom% V, and then decreases again to a very low value of the V_2O_5-alone catalyst, with an increase in the V_2O_5 content. The direction of this change is the same as that of the basicity of the catalysts shown in Fig. 3. A proportional relationship was obtained between r_P and the acidity, i.e., the amount of pyridine required to poison the isomerization activity (Fig. 5).

5. *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 acidity of the catalyst in Fig. 5. A proportional relationship was also obtained between the activity and the acidity. The product ratio of *cis-/trans*-2-butene was 1–2.

6. *Oxidation Activity for Butadiene*

Butadiene was oxidized in an excess of air over the series of SnO_2–V_2O_5 catalysts

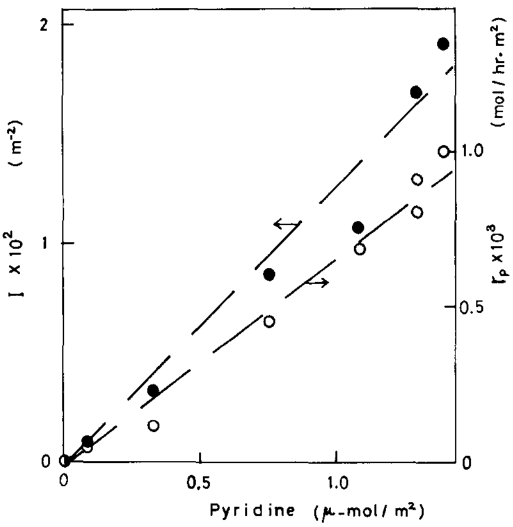

FIG. 5. The isomerization activity for 1-butene and the dehydration activity for IPA as a function of the acidity (amount of pyridine required to poison the isomerization of 1-butene): (○) dehydration; (●) isomerization.

by changing the amounts from 1.0 to 25 g. The initial rate of the overall consumption of butadiene at 290°C, r_B (mol/hr·m^2-cat) was adopted, for convenience in the experimental procedures, as a measure of the activity for the basic reactant; it is plotted as a function of the catalyst composition in Fig. 6. The r_B increases monotonously with the V_2O_5 content up to about 50 atom% V, approaching the value of pure V_2O_5.

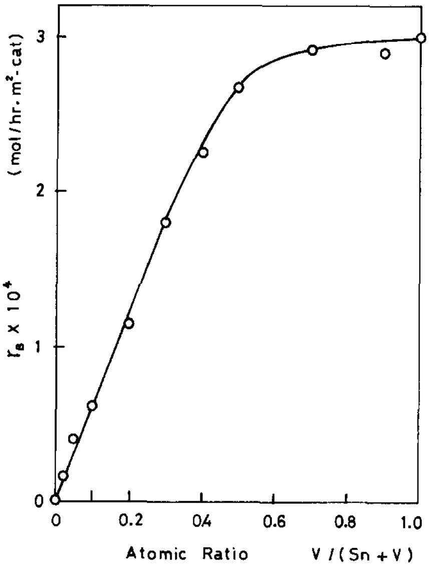

FIG. 6. The oxidation activity for butadiene as a function of the V_2O_5 content.

7. *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 product (*8,11,12*):

Type 1: basic reactant ⟶ acidic product,

Type 2: basic reactant ⟶ basic product.

As a reaction of Type 1, the oxidation of butadiene to maleic anhydride in the presence of excess air (0.67 mol% C_4H_6) was chosen. The selectivity at a conversion of about 40–50% was measured for every catalyst; it is plotted as a function of the catalyst composition in Fig. 7. The selectivity to maleic anhydride increases sharply with the acidity in the range of V = 10–40%.

On the other hand, as an example of the

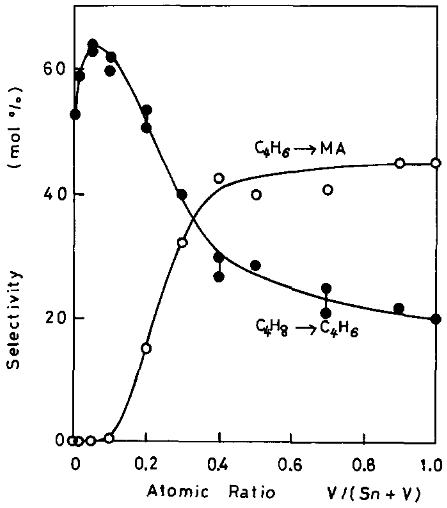

FIG. 7. Selectivity versus the V_2O_5 content: (○) selectivity of butadiene to maleic anhydride; (●) selectivity of 1-butene to butadiene.

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 plotted in Fig. 7. The selectivity to butadiene passes through a maximum at about 5 atom% V and then decreases when the V_2O_5 content increases further.

DISCUSSION

These experiments first show that the incorporation of V_2O_5 to SnO_2 induces a remarkable increase in the surface area, which directly contributes to the catalytic activity.

Next, the incorporation of V_2O_5 modifies, to a significant extent, the acid–base properties of the system. In a V_2O_5-poor composition ($V < 20$ atom%), the catalysts are basic, while the catalyst containing more than 40 atom% V are acidic. It should be noted that, although V_2O_5 is a typical acidic element, the incorporation of a minor amount of ($V = 2$–20 atom%) V_2O_5 to SnO_2 remarkably enhances the basicity, and that the incorporation of V_2O_5 to SnO_2 never enhances the acidity per unit of the surface area more than V_2O_5 itself, unlike the cases of V_2O_5–MoO_3 (*9*) and SnO_2–MnO_3 (*17*).

The freshly prepared SnO_2–V_2O_5 catalysts have a color varying from light gray to orange-yellow with an increase in the V_2O_5 content, though the binary oxides are a little more bluish than the pure V_2O_5. By the use in the oxidation reaction, the catalysts are dark colored, as a result of the partial reduction of the metal oxides. The extent of the reduction seems to depend largely on the concentrations of the reactants and oxygen and the temperature. The reduced catalysts can be returned to their oxidized states, to some extent, by the heat treatment in flowing air at 500°C. In order to know how the oxidation states of catalyst affect the acid–base properties, we compared, in the cases of several catalysts, the NH_3 amount adsorbed on the catalysts used in the oxidation of 1-butene at 250°C for 30 min (in reduced states) with that adsorbed on the heat-treated catalysts (in oxidized states), but no clear difference was observed.

A comparison of the catalytic activities for IPA with the acidity–basicity data reveals that the activity for the dehydration to propylene represents the acidity and that the value of the r_a/r_p ratio is also valid enough as a rough index of the basicity. Therefore, this indirect method based on the catalytic activity may be recommended, especially in the cases of catalysts whose surface areas are too small for the amount of adsorption to be measured.

The proportional relationship between the activity for the isomerization of butene and the acidity of the catalysts and the independence of the activity from the basicity and the product ratio of *cis*-/*trans*-2-butene (*12,18*) indicate that, under the cirsumstances of the oxidation reaction, the isomerization is catalyzed only by the acidic sites. 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 or other acidic products under the circumstances of the oxidation.

Though both the activity for butadiene oxidation, r_B, and the acidity increase as the V_2O_5 content increases (Figs. 2 and 6), the shapes of these two curves are not exactly the same. That is, the addition of a relatively small amount of V_2O_5 to SnO_2 ($V < 20$ atom%) induces little increase in the acidity, but a sharp increase in the oxidation activity results. To explain this difference, we envisage (*8*) that when the catalyst is highly acidic and scarcely basic, much as in the V_2O_5–P_2O_5, V_2O_5–MoO_3, and MoO_3–P_2O_5 catalyst systems, the oxidation activity for such basic reactants as olefins is controlled only by the activation of olefin, which is performed at the acidic sites of the catalyst. However, as the acidic property decreases and as the basic property increases, the contribution of the acidic sites decreases, while that of the activation of oxygen, which is connected, presumably, with the number of basic sites on the surface of the catalyst as well as with their oxygen mobility (*12*), increases. Practically, in the case of oxidation over such scarcely acidic catalysts as the Ni, Co, Cr, and Cu metal oxides, the activity must be controlled entirely by the activation of surface oxygen—that is, by the oxidizing power of surface oxygen (*12,19*).

Therefore, it may be speculated that, when the V_2O_5 content is low and the catalysts are moderately acidic, the oxidation of olefin is affected to a considerable extent by the activation of oxygen. However, as the V_2O_5 content increases, the contribution of acidic sites increases, and when the V_2O_5 content is high and when the catalyst becomes highly acidic, the reaction is controlled mainly by the acidic sites.

With regard to the selectivity, the character of the maleic anhydride curve in Fig. 7 is quite similar to that of the acidity (shown in Fig. 2). This supports the consideration (*8,11–15*) that a requirement for an effective catalyst in this type of reaction is the acidic property; this may be concluded for two reasons: (a) the acidic catalyst is active for the oxidation of the reactant, and (b) it is inactive for the degradation of the acidic compound produced. On the other hand, the character of the curve of the butadiene formation resembles that of the basicity of the catalysts. This reveals that, as the basic property of SnO_2 is not very strong, the catalysts of an enhanced basicity and those of a relatively low acidity are favorable for the selectivity of this type of reactions. When the acidic character is too high, butadiene is oxidized more rapidly than butene, because butadiene is more basic than butene (the ionization potential of butadiene [8.75–9.18 eV] is lower than that of butene [9.3–9.8 eV]).

The SnO_2–V_2O_5 catalyst containing about 50 atom% V has been reported to be effective in the oxidation of butene to acetic acid (*2,20,21*). The requirements of an effective catalyst for this oxidation may be: (a) that the catalyst is acidic, i.e., active enough even at low temperatures, because acetic acid is decomposed easily compared with maleic anhydride (*15,21*), and (b) that it has acidic sites of an acid strength high enough to be active for the C–C fission of butene (*15*). The results of this study reveal that the acidity per unit of weight is maximum at the V content of about 50 atom%. Taking into account the fact that the nature of active sites, i.e., the acid strength, is not changed with a change in the catalyst composition (*12*), it can be understood that the catalyst of V = about 50 atom% is optimal for this reaction.

It can be concluded that the oxidation activity and selectivity of the SnO_2–V_2O_5 catalysts are interpreted in connection with the acid–base properties which are strongly changed by the catalyst composition.

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