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

II. The SnO_2–MoO_3 and SnO_2–P_2O_5 Systems

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The vapor-phase oxidation of 1-butene, butadiene, and acetic acid, 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, over two series of catalysts, SnO_2–MoO_3, and SnO_2–P_2O_5, and the relationship between the catalytic behavior and the acid–base properties of the catalysts was investigated. The acidity and the basicity of the SnO_2–MoO_3 catalysts were measured by studying the adsorption of basic and acidic molecules, respectively, in the gas phase, using both the static and pulse methods. The acidities of the SnO_2–MoO_3 catalysts are dramatically high at the Mo content of 30–60 atom%, though those of the SnO_2-rich (Mo < 20 atom%) and MoO_3-rich (Mo > 80 atom%) catalysts are fairly low. The basicity is remarkably enhanced by the introduction of a small amount of MoO_3 (Mo < 5 atom%). It can be said that the catalysts are basic in the MoO_3-poor composition. In the case of the SnO_2–P_2O_5 catalysts, the acidity and basicity were evaluated from the catalytic activity for the dehydration of IPA to propylene and the (dehydrogenation rate for IPA)/(dehydration rate for IPA) ratio, respectively. The introduction of P_2O_5 increases the acidity and decreases the basicity, to a very small extent, so it cannot cause a remarkable modification in the catalytic behavior; that is, the SnO_2–P_2O_5 catalysts are rather basic.

INTRODUCTION

The present paper is the second part of an investigation of the catalytic activity of the SnO_2-based binary catalysts. In the preceding paper (*1*) we reported on the SnO_2–V_2O_5 system. It was found that the catalytic behavior, which changes remarkably with the catalyst composition, can be explained by the acid–base properties of the catalysts. We now deal with the SnO_2-based catalysts combined with other acidic elements, such as MoO_3 and P_2O_5, and attempt to explain the characteristic catalytic action of these two catalyst systems in terms of their acid–base properties.

EXPERIMENTAL METHODS

Two series of binary catalysts of SnO_2–MoO_3 and SnO_2–P_2O_5, with different compositions, were prepared by the procedures described in the preceding work (*1*). The starting materials used for the second components were $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and 85 wt% H_3PO_4.

The acidity and basicity of the catalysts were measured by means of the adsorption of basic and acidic molecules, respectively, in the gas phase, using both the static and pulse methods. The technique of the measurement has also been described in earlier works (*1,2*).

The vapor-phase oxidation of 1-butene, 1,3-butadiene, and acetic acid, and the dehydration and dehydrogenation of isopropyl alcohol (IPA) were carried out in an ordinary continuous-flow-type reaction system. The reactor and the experimental and analytical procedures were the same as those employed in our previous works (*1–7*).

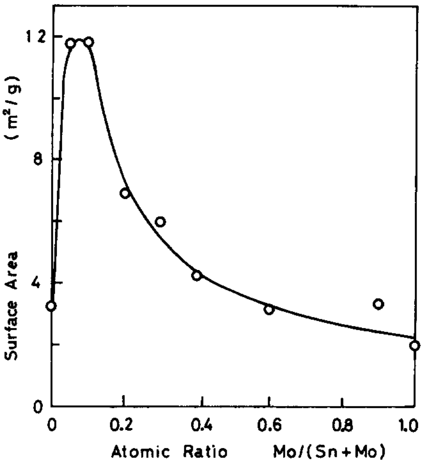

FIG. 1. Effect of the MoO_3 content on the surface area.

RESULTS AND DISCUSSION

A. The SnO_2–MoO_3 System

1. *Surface Area*

The effect of the catalyst composition on the specific surface area was first examined by the BET method, using nitrogen at −195°C. The results are shown in Fig. 1. As the MoO_3 content increases, the surface area increases sharply; it passes through a maximum at Mo = 5–10 atom%.

2. *Acidity*

The acidity per unit of the surface area of the SnO_2–MoO_3 catalysts, as determined by the amount of NH_3 irreversibly adsorbed at 250°C and 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 content in Fig. 2. A parallelism was found between the amounts of NH_3 obtained by means of the pulse method; this finding may support the validity of these results. The values of NH_3 is always greater than that of pyridine. NH_3 can be adsorbed even at 250°C on the acidic sites of a weak acid strength, which cannot catalyze the isomerization of butene.

The results indicate that the acidity is fairly low in the low range of the MoO_3 content (Mo < 20 atom%), but that it increases rapidly with the MoO_3 content, shows a maximum at about Mo = 30–60 atom%, and then decreases again to a very low value of pure MoO_3. It should be noted that the acidity of the catalysts containing 30–60 atom% Mo is dramatically high, the highest of the many kind of binary oxides examined by us, such as V_2O_5–MoO_3, P_2O_5, WO_3, SnO_2, TiO_2, and Fe_2O_3 and MoO_3–P_2O_5, WO_3, TiO_2, and Fe_2O_3 (*1*–*5*).

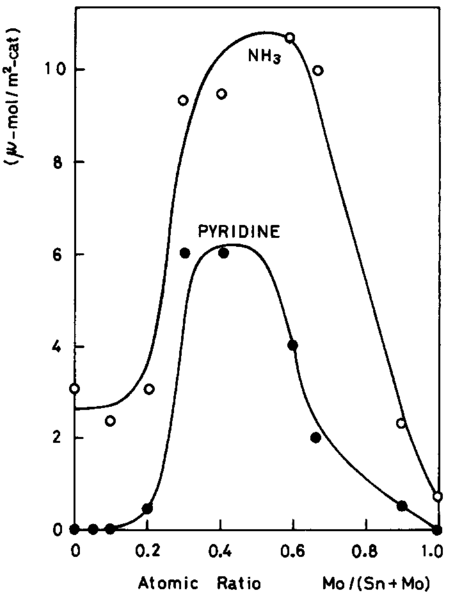

FIG. 2. Acidity of SnO_2–MoO_3 as a function of the MoO_3 content: (○) NH_3 at 250°C (static method); (●) pyridine required to poison the isomerization activity for 1-butene at 160°C (pulse method).

3. *Basicity*

The basicity per unit of the surface area of the SnO_2–MoO_3 catalysts, as determined by the irreversible adsorption of acidic molecules in the gas phase, is shown in Fig. 3 as a function of the MoO_3 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 MoO_3 content. The dif-

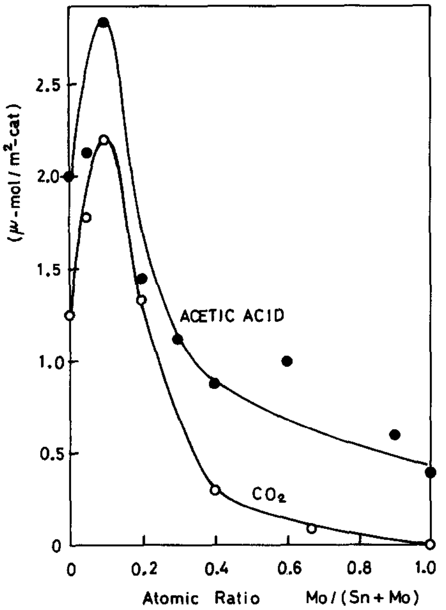

FIG. 3. Basicity of SnO_2–MoO_3 as a function of the MoO_3 content; (○) CO_2 at 20°C (static method); (●) acetic acid at 130°C (pulse method).

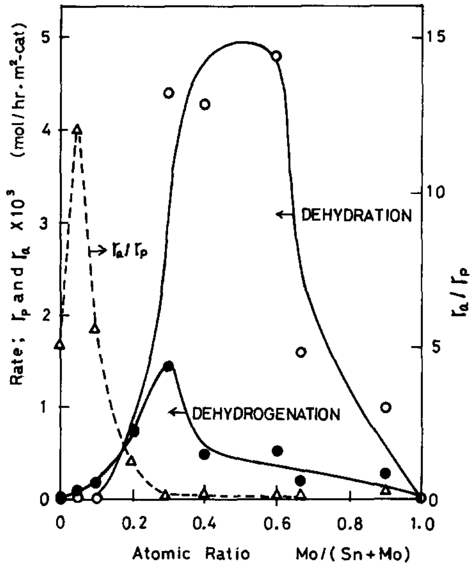

FIG. 4. The dehydration and dehydrogenation activities for IPA, r_p and r_a, and the r_a/r_p ratio, versus the MoO_3 content: $T = 175°C$, IPA = 1.65 mol% in air.

ference may be mainly attributed to the difference in the acid strength between CO_2 and acetic acid, and acetic acid may be adsorbed on the basic sites of a lower base strength than CO_2.

It is evident that, with an increase in the MoO_3 content, the basicity sharply increases at first, passes through a maximum at about Mo = 10 atom%, and then decreases to the very low value of the pure MoO_3 catalyst, much as in the case of SnO_2–V_2O_5 catalyst system (*1*).

4. *Dehydration and Dehydrogenation Activities for IPA*

In order to examine whether or not the catalytic activity for the dehydration and the (dehydrogenation rate)/(dehydration rate) ratio in the reaction of IPA really represent the true values of the acidity and basicity of the catalysts, the reaction of IPA was performed in an atmosphere of air. The initial rates of the dehydration and the dehydrogenation at 175°C, r_p and r_a (mol/hr·m²-cat), are plotted, together with the r_a/r_p ratio, in Fig. 4.

As the MoO_3 content increases, the values of r_p and r_a/r_p ratio vary in the same direction as the acidity and basicity (Figs. 2 and 3, respectively). It should also be noted that the catalysts containing 30–60 atom% Mo have a significantly high activity for the dehydration of IPA.

5. *Isomerization Activity for Butene*

The isomerization of 1-butene was carried out at 0.67 mol% C_4H_8 in air and at 225°C by changing the catalyst amounts in the range of 1–20 g; the (*cis*-2-C_4H_8 + *trans*-2-C_4H_8)/(1-C_4H_8 + *cis*-2-C_4H_8 + *trans*-2-C_4H_8) ratio corresponding to 1 m² of the catalyst, *I*, was adopted as a measure of the activity. The results are plotted in Fig. 5. The isomerization activity changes in a manner similar to the acidity shown in Fig. 2.

6. *Oxidation Activity for Butadiene*

Butadiene was oxidized in an excess of air, and the initial rate of the overall con-

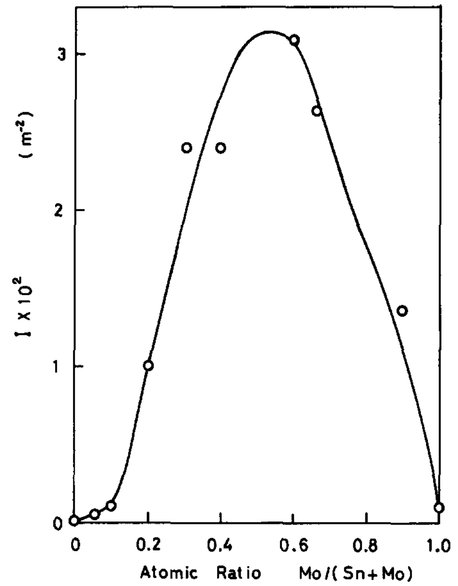

FIG. 5. The isomerization activity for 1-butene as a function of the MoO_3 content.

sumption of butadiene at 320°C, r_B (mol/hr·m²-cat) was plotted as a function of the MoO_3 content in Fig. 6. The r_B increases steadily with the MoO_3 content and attains a maximum at Mo = 40 atom%. But the trend of the r_B curve is a little different from that of the acidity.

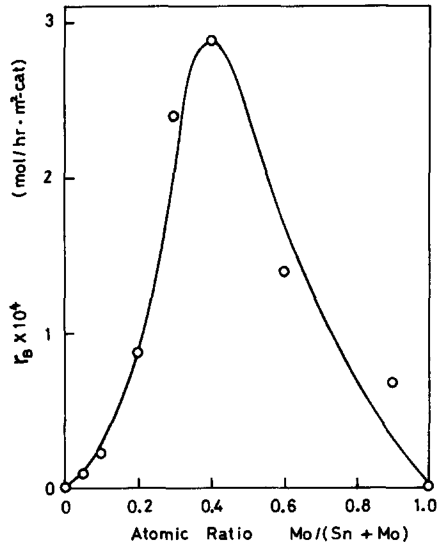

FIG. 6. The oxidation activity for butadiene as a function of the MoO_3 content.

7. Selectivity in Oxidation of Olefin

In a manner similar to those in previous studies, the selectivities for the two types of oxidation were examined (*1–3,6,7*). As a model of the "base to acid" reactions, the oxidation of butadiene to maleic anhydride was chosen; the selectivity at conversion of about 40–50 mol% is shown in Fig. 7. On the other hand, as an example of the "base to base" reactions, the oxidation of 1-butene to butadiene at the concentrations of $O_2 = 0.34–1.3$ mol% and $C_4H_8 = 0.67$ mol% was chosen; the selectivity at a conversion of about 30–40% is plotted in Fig. 7. The trends of the curves of maleic anhydride and butadiene resemble those of the acidity and basicity, respectively.

8. Discussion

The incorporation of MoO_3 into SnO_2 modifies the acid–base properties to a significant extent, as well as the surface area. In a MoO_3-poor composition (Mo < 20 atom%), the catalysts are basic, while the

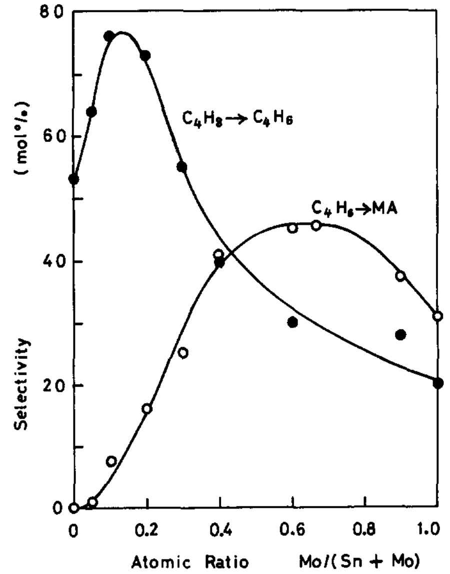

FIG. 7. Selectivity vs the MoO_3 content: (○) selectivity of butadiene to maleic anhydride; (●) selectivity of 1-butene to butadiene.

catalysts containing more than 30 atom% Mo are acidic. It is noteworthy that, though MoO_3 is a typical acidic element, the incorporation of a small amount (Mo $<$ 5 atom%) remarkably increases the basicity, much as in the case where V_2O_5 was combined with SnO_2 (*1*), and that the catalysts containing 30–60 atom% Mo have a dramatically high acidity compared with other binary metal-oxide systems.

The freshly prepared SnO_2–MoO_3 catalysts are almost light yellowish gray color. However, the catalysts used for the reactions of butene, butadiene, IPA, and acetic acid are dark colored, due to the partial reduction of the metal oxides, whose extent seems to depend on the concentrations of the reactants and oxygen and the temperature. Practically, the used catalysts of Mo = 5–33 atom% are real black. The reduced catalysts cannot be returned completely to their initial color even by a heat treatment at 500°C in flowing air. From the color of the catalysts, it seems that the oxidation states of the catalysts, especially used in the oxidation reactions, are greatly changed with the composition, and that the more liable to change into the reduced states during the oxidation reactions the catalysts are the higher in the acidity. So we tried to compare 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), in order to examine the effect of the oxidation states on the acid-base properties. However, no clear difference was observed.

The results obtained in the reactions of IPA prove that the values of r_p and the r_a/r_p ratio are effective as rough measures of the acidity and the basicity of a catalyst, respectively, much as in the cases of the SnO_2–V_2O_5 (*1*) and MoO_3–Bi_2O_3–P_2O_5 systems (*2*).

The isomerization activities for butene are correlated only with the acidity, not with the basicity, and the product ratio of *cis-/trans*-2-butene is 1–2. This evidence proves that, under the circumstances of the oxidation, the isomerization is catalyzed only by the acidic sites (*8*) and that the contribution of the basic sites is not important.

The similarity of the r_B curve (Fig. 6) to the acidity curves (Fig. 2) suggests that the acidic sites play an important role in the oxidation, probably in the activation of the olefin (*1–7*). However, the shapes of these curves are not exactly the same; the addition of a small amount of MoO_3 (Mo $<$ 20 atom%) induces little increase in the acidity, but it does induce a steady increase in the oxidation activity. This implies a contribution of another factor, that is, the activation of oxygen, which is presumably connected with the amount and the oxygen mobility of the basic sites (*2*). The fact that the oxidation activity of the SnO_2–MoO_3 system is much lower than that of the SnO_2–V_2O_5 system, though the former has a much higher acidity than the latter, may also support the participation of the factor relating to the activation of surface oxygen.

Taking into account the fact that the basic property of SnO_2 itself is not very strong, the results of the selectivity (Fig. 7) support our opinion that a requirement for an effective catalyst in the acid-formation reactions is an acidic character, while the requirement for a catalyst in the base-formation reactions is a moderate character both in an acid and a base (*1–7*).

The SnO_2–MoO_3 system has been reported to be effective in acetone formation from propylene (*9,10*). Why is SnO_2–MoO_3 the sole catalyst giving acetone in a high yield? To answer this important question, we would like to propose that the selectivity-controlling factor is the consecutive decomposition of the acetone produced which is enhanced markedly at a

TABLE 1
INFLUENCE OF THE P_2O_5 CONTENT ON THE PROPERTIES AND ACTIVITY OF SnO_2–P_2O_5 CATALYSTS[a]

P_2O_5 content (atom%)	0	5	10	20
Surface area (m^2/g)	3.3	2.8	3.0	2.1
$r_p \times 10^4$ (mol/hr · m^2)	0.46	0.47	1.9	1.5
r_a/r_p	3.4	0.9	0.22	0.26
$r_B \times 10^5$ (mol/hr · m^2)	2.4	3.3	5.0	6.7
$r_A \times 10^5$ (mol/hr · m^2)	4.7	1.3	0.8	1.0
Selectivity of C_4H_6 to maleic anhydride (mol%)	0	0	0	0
Selectivity of 1-C_4H_8 to C_4H_4 (mol%)	53	55–60	77–82	70

[a] r_p and r_a, dehydration and dehydrogenation rates of IPA at 265°C and 1.65 mol% IPA in air; r_B, rate of overall consumption of butadiene at 390°C and 0.67 mol% butadiene in air; r_A, rate of oxidation of acetic acid to CO_2 at 315°C and 1.5 mol% acetic acid in air; selectivity to maleic anhydride, at conversion of 40–50%; selectivity to butadiene, at conversion of 30–40%.

high temperature; therefore, the dramatically high acidity of SnO_2–MoO_3 and also the basicity, which serves to further the dehydrogenation of intermediate IPA, enable the reaction to take place at very low temperatures.

B. The SnO_2–P_2O_5 System

The results obtained from the SnO_2–P_2O_5 catalysts are listed in Table 1.

The introduction of P_2O_5 to SnO_2 induces a small decrease in the specific surface area. As the surface areas were small, we measured the values of r_p and the r_a/r_p ratio at 265°C as indices representing the acidity and the basicity, respectively. With an increase in the P_2O_5 content from 0 to 20 atom%, the acidity, r_p, increases and the basicity, r_a/r_p, decreases to a small extent, as had been expected. With regard to the oxidation activity, the activity for butadiene, r_B, which is very low compared with that of the SnO_2–V_2O_5 and SnO_2–MoO_3 systems, increases, while the activity for acetic acid, r_A, decreases. These changes in the oxidation activity can be understood in terms of our conception that the oxidation activities for the basic (olefin) and acidic reactants are activated at the acidic and basic sites, respectively (*1–7*). The selectivity in the oxidation of 1-butene to butadiene increases from 53 to 70–80 mol% upon the addition of P_2O_5. This increase may be due to the fact that pure SnO_2 does not have an acidic character sufficient even for such a kind of reaction, though TiO_2 is considered to be a little more acidic than SnO_2, showing the higher selectivity of about 80 mol% (*5*). On the other hand, maleic anhydride is not formed at all in the oxidation of butadiene. As the value of r_p indicates, the SnO_2–P_2O_5 catalysts are very low in acidity. It has previously been pointed out by us that acidic products can be obtained uniquely by "the highly acidic catalysts" (*1–7*).

These results indicate that the introduction of P_2O_5, which is also a typical acidic element but which has no oxidizing power, changes the acid–base properties to only a small extent; therefore, it cannot cause a remarkable modification in their catalytic behavior. That is, the SnO_2–P_2O_5 catalysts keep the characteristics of pure SnO_2; they are rather basic catalysts. This may be one of the reasons why the SnO_2–P_2O_5 catalyst is effective for the oxidation of ethylbenzene to styrene (*11*), one of the "base to base" reactions. It should also be noted that, unlike as in other metal oxides such as MoO_3 and V_2O_5, the introduction of P_2O_5 decreases the surface area, much as in the cases of the MoO_3–P_2O_5 (*12*) and V_2O_5–P_2O_5 (*4*).

It can be concluded that the acid–base conception that the catalytic activities are governed by the acid–base properties between the catalyst and the reactant is still effective in explaining the function of MoO_3 and P_2O_5 added to SnO_2.

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