Oxidation Activity and Acid-base Properties of Mixed Oxide Catalysts Containing Titania. II. The TiO_2–V_2O_5–P_2O_5 System

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The acidity and basicity of a series of TiO_2–V_2O_5–P_2O_5(atomic ratio Ti : V : P=9 : 1 : x)catalysts with different P_2O_5 contents (x=0—18), were measured by studying the adsorption of the basic and acidic molecules in the gas phase, using both the static and pulse methods. TiO_2–V_2O_5(V/Ti=1/9) is rather basic, but this catalyst can be modified from basic to acidic by the introduction of P_2O_5. The vapor-phase oxidation of butadiene and 1-butene, which were chosen as electron-donor-type reactants, and that of acetic acid, as an acidic reactant, were carried out in the presence of an excess of air, and then the relationship between the catalytic behavior and the acid-base properties was investigated. The results support an earlier proposal that the activity and selectivity in mild oxidation can be interpreted in terms of the acid-base properties of the catalyst and the reactant.

TiO_2 is an amphoteric oxide and its acid-base properties are significantly modified by the introduction of a small quantity of additive.[1,2] The acidic sites and electron donating sites of TiO_2 and their variation with pretreatment or in combination with several oxides have also been studied, in connection with active sites for the isomerization of butene, by Tanabe *et al.*[3–5]

In a preceding report,[6] the acid-base properties of TiO_2–V_2O_5 and TiO_2–MoO_3 binary systems and their correlation with oxidation activities were studied. It was found that the basic character of the systems is greatly enhanced by the addition of a small amount of such acidic elements as MoO_3 and V_2O_5 to TiO_2 and, therefore, the binary systems are sufficiently basic at Mo<20 or V<10 atom%. On the other hand, it has been reported that (1) the addition of P_2O_5 to TiO_2 sharply increases the acidity,[1] unlike the case in which P_2O_5 is added to SnO_2,[7] and that (2) TiO_2–P_2O_5 catalysts containing a large amount of P_2O_5 are highly acidic and are active as polymerization catalysts.[8]

This evidence led to the prediction that the acid-base character of TiO_2-containing mixed oxide catalysts can be modified by controlling the amounts of either the V_2O_5 or the P_2O_5 added.

The present paper is the second part of an investigation of the oxidation activity of the TiO_2-based catalysts. An attempt was made to ascertain how the addition of various amounts of P_2O_5 to TiO_2–V_2O_5 (amount ratio V/Ti=1/9) modifies the acid-base properties and how these properties are correlated with the oxidation activity and selectivity.

Experimental

Catalysts. The catalysts used in this study were of the TiO_2–V_2O_5–P_2O_5 series (atomic ratio Ti : V : P=9 : 1 : x), with eight different amounts of P_2O_5 (x=0—18). They were prepared by the procedures described in a preceding report.[6]

Procedures. The acidity of the TiO_2–V_2O_5–P_2O_5 catalysts were determined both by the amount of NH_3 irreversibly adsorbed (static method) and by that of the pyridine required to completely poison the isomerization activity for 1-butene (pulse method). The basicity was determined by the amount of CO_2 irreversibly adsorbed, using the static method. The technique used in these measurements has also been described earlier.[6,7,9)

The vapor-phase oxidation of 1-butene, 1,3-butadiene, and acetic acid and the isomerization of 1-butene were carried out in the presence of an excess of air, in an ordinary continuous-flow-type reaction system. The reactor and the experimental procedures were the same as those employed previously.[1,6,7,9]

Results

Surface Areas. The surface areas of the TiO_2–V_2O_5–P_2O_5 catalysts were checked by the BET method using nitrogen at −196 °C. The results are shown in Table 1. The surface area increases gradually for an increase in the P_2O_5 content (x), but decreases when the P_2O_5 content becomes too high (x=18).

Acidity. The acidity per unit surface area of the TiO_2–V_2O_5–P_2O_5 catalysts, as determined by the amounts of NH_3 irreversibly adsorbed at 20, 200, and 250 °C, are plotted in Fig.1 as a function of the P_2O_5 content (x). These results indicate that the P_2O_5-poor catalysts have a fair amount of acidic sites of weak acid strength, as has been pointed out in a previous paper.[6] The acidity obtained by the amount of pyridine required to completely poison the isomerization activity for 1-butene at 160 °C is also plotted in Fig. 2. 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, which proves the validity of these results.

It is found, as was expected, that the acidity of TiO_2–V_2O_5–P_2O_5 catalysts increases for an increase in the P_2O_5 content.

Basicity. The basicity per unit surface area of the TiO_2–V_2O_5–P_2O_5 catalysts, as determined by the amount of CO_2 irreversibly adsorbed at 20 °C, is plotted in Fig. 3 as a function of the P_2O_5 content (x). It is also demonstrated that the basicity of the catalysts

TABLE 1. SURFACE AREA OF THE TiO_2–V_2O_5–P_2O_5 (atomic ratio Ti : V : P=9 : 1 : x) CATALYSTS USED

P_2O_5 content x	Surface area (m^2/g)	P_2O_5 content x	Surface area (m^2/g)
0	23.8	2.0	39.1
0.2	24.0	4.0	42.4
0.5	35.0	9.0	46.2
1.0	37.3	18.0	25.3

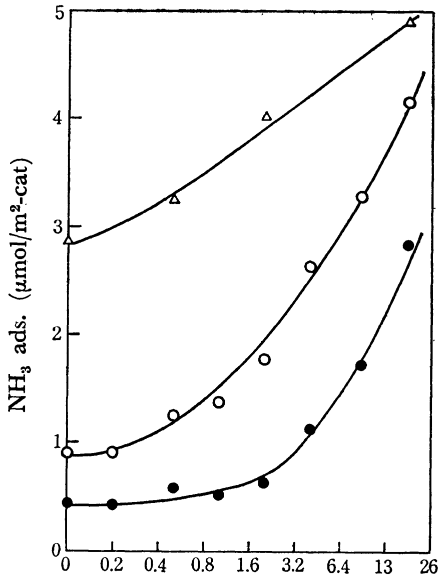

Fig. 1. Acidity of TiO_2-V_2O_5-P_2O_5 (9 : 1 : x) as a function of the P_2O_5 content (x). I. Irreversible adsorption of NH_3 at 20 °C: △, at 200 °C: ○, at 250 °C: ●.

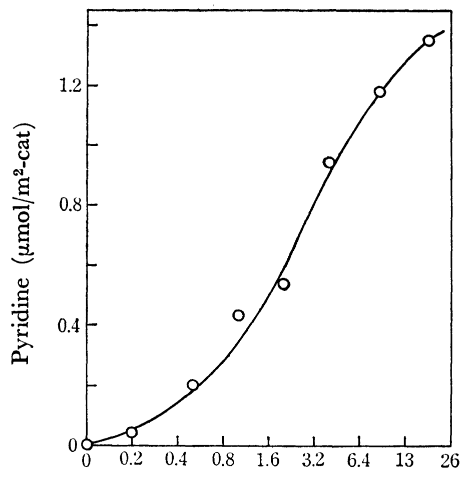

Fig. 2. Acidity of TiO_2-V_2O_5-P_2O_5 (9 : 1 : x) as a function of the P_2O_5 content (x). II. Pyridine required to poison the isomerization activity for 1-butene at 160 °C (pulse method).

gradually decreases for an increase in the P_2O_5 content.

Isomerization Activity for Butene. The relationship between the catalytic activity for isomerization and the acid-base properties was investigated. The reaction was carried out at 0.67 mol% 1-butene in air and at 250 °C by changing the catalyst amounts in the range of 1.0 to 10 g. As a measure of the isomerization activity, the ratio of (*cis*-2-butene+*trans*-2-butene)/(1-butene+*cis*-2-butene+*trans*-2-butene) corresponding to 1 m^2 of the catalyst, I, was adopted, much as in the cases reported previously.[6,7,9]

The results are plotted in Fig. 4 as a function of the acidity of the catalyst, *i. e.*, the amount of pyridine required to poison the isomerization activity. A roughly proportional relationship was obtained between the isomerization activity and acidity.

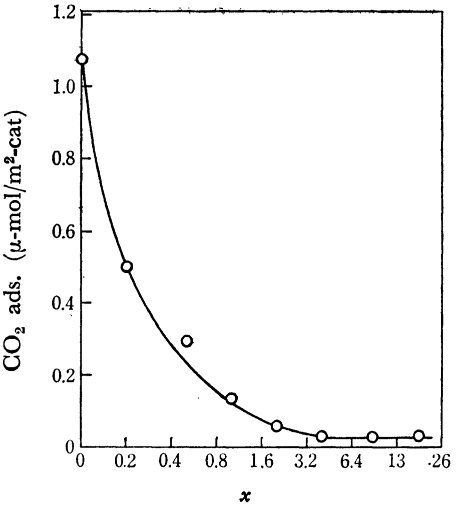

Fig. 3. Basicity of TiO_2-V_2O_5-P_2O_5 (9 : 1 : x) as a function of the P_2O_5 content (x). Irreversible adsorption of CO_2 at 20 °C.

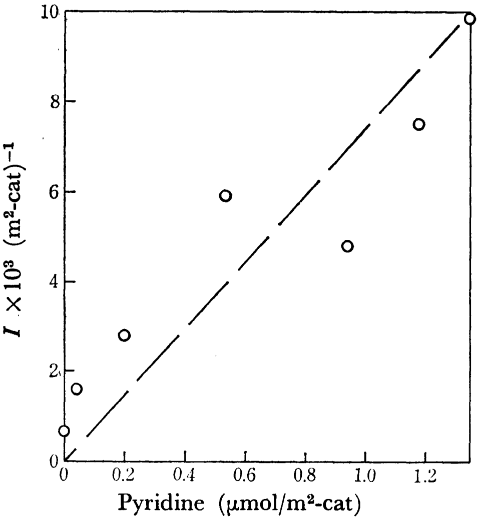

Fig. 4. Relation between the isomerization activity for 1-butene (I) and the acidity (amount of pyridine required to poison the isomerization of 1-butene). $I=(cis\text{-}2\text{-}C_4H_8+trans\text{-}2\text{-}C_4H_8)/(1\text{-}C_4H_8+cis\text{-}2\text{-}C_4H_8+trans\text{-}2\text{-}C_4H_8)$ corresponding to 1 m^2 of the catalyst, T=250 °C, 1-C_4H_8=0.67 mol% in air.

Oxidation Activity for Olefin. Butadiene was chosen as an electron-donor-type (basic) reactant and was oxidized in an excess of air (0.67 mol% of butadiene in air) by changing the amounts of the catalyst from 3 to 20 g. The initial rate of the overall consumption of butadiene at 295 °C, r_B (mol/h m^2-cat), was adopted as a measure of the oxidation activity, much as in the cases reported previouly.[6,7,9] This is plotted in Fig. 5 as a function of the P_2O_5 content (x).

The activity first increases with the P_2O_5 content, reaches a maximum at about x=0.4, and then decreases again to a very low value.

Oxidation Activity for an Acidic Compound. Acetic acid was chosen as the acidic reactant, and it was oxidized in an excess of air (1.5 mol% of acetic acid

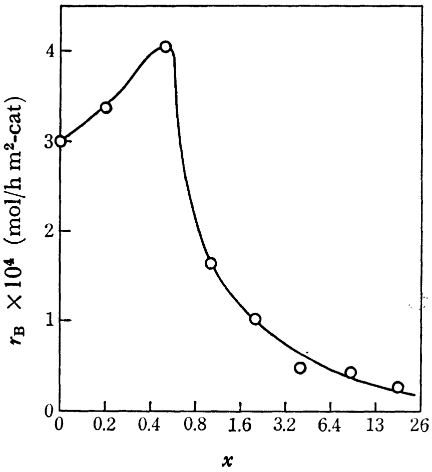

Fig. 5. The oxidation activity for butadiene (r_B) as a function of the P_2O_5 content (x).
Butadiene = 0.67 mol% in air, T = 295 °C.

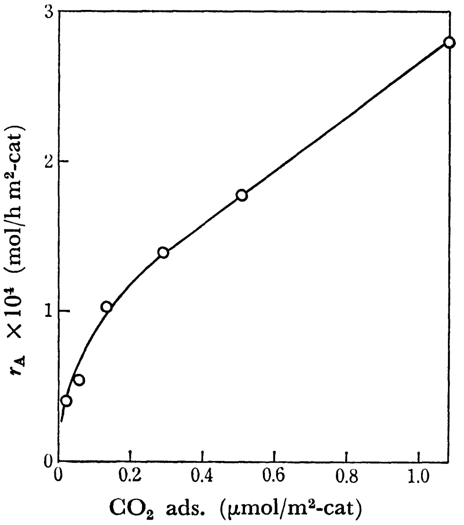

Fig. 6. Relation between the oxidation activity for acetic acid (r_A) and the basicity (amount of CO_2 irreversibly adsorbed).
Acetic acid = 1.5 mol% in air, T = 325 °C.

in air). The initial rate of oxidation to CO_2 at 325 °C, r_A (mol/h m^2-cat), was adopted as a measure of the oxidation activity. It is plotted in Fig. 6 as a function of the basicity of the catalyst, *i. e.*, the amount of CO_2 irreversibly adsorebed. The activity steadily increases with an increase in the basicity of the catalyst.

Selectivity in the Oxidation of an Olefin. The partial oxidation reactions are divided into two types in terms of the acid-base properties of the products:[1,6,7,9,10]

Type 1: Basic reactant→acidic product

Type 2: Basic reactant→basic product

Both the selectivity of butadiene to maleic anhydride at 40—50% conversion and that of 1-butene to butadiene at 30—40% conversion, which were chosen as model reactions of Types 1 and 2, respectively, are plotted in Fig. 7 as a function of the P_2O_5 content (x).

The results indicate that the "base-formation" reaction is favored by a rather basic catalyst and that the "acid-formation" reaction is favored by an acidic catalyst, as expected on the basis of earlier studies.[1,6,7,9,10]

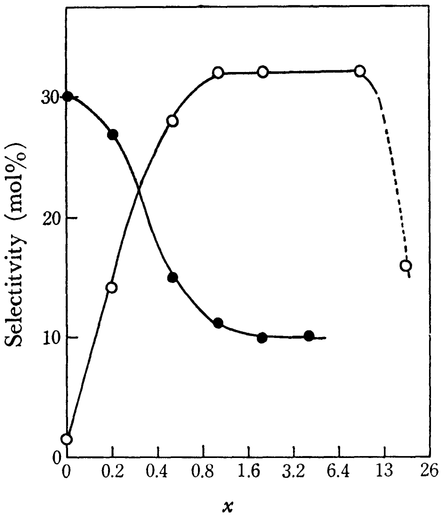

Fig. 7. Selectivity as a function of the P_2O_5 content (x).
○: Selectivity of butadiene to maleic anhydride, ●: selectivity of 1-butene to butadiene.

Discussion

Generally speaking, to be active in oxidation reactions, a catalyst must participate in the following two processes:

(1) activation of reactant molecules, and

(2) activation of oxygen.

When a catalyst is potent in the activation of oxygen, *i. e.*, has an oxidizing power which depends on two factors: (a) the number of oxidizing sites, and (b) the mobility of oxygen at a site, the oxidation reaction takes place without requiring activation of the reactant, therefore, the catalytic activity is controlled only by the activation of oxygen and the reaction proceeds non-selectively toward CO_2 and H_2O. This is the case of deep oxidation over such metal oxides as NiO, Co_3O_4, Cr_2O_3, MnO_2, and CuO. On the other hand, when the oxidizing power of a catalyst is not so strong, the reaction requires activation of the reactant as well as of oxygen, and, therefore, the difference in the mode or degree of this reactant-activation brings about the selectivity of the catalyst. Thus, it can be said that a requirement for an effective catalyst for any selective oxidation is a "moderate" oxidizing power, as has been pointed out by Sachtler *et al.*[11]

In studies on selective oxidations, many attempts have been made to disclose the active component in mixed oxide catalysts and to interpret the catalytic behaviors in connection with a particular structure (including electronic structure) of the metal oxides, as has been reviewed.[12]

Recently, the present author has proposed, from a different point of view, that it is the acid-base properties of the catalyst as well as the oxygen mobility which are directly responsible for the catalytic actions, although a change in the structure may naturally cause a change in these properties.[6,7,9,10] The acidic sites, probably consisting of metal ions with a particularly high electron affinity, play a role in electron transfer from the reactant of the sites, resulting in the formation of a cationic intermediate and a reduced metal ion,[13] *i. e.*, the acidic sites contribute to the activation of the reactant. On the other hand, the basic sites, owing to their ability to donate electron to oxygen, contribute to adsorb and activate the gaseous oxygen and also to reoxidize the reduced metal ions, that is, the basic sites are connected with the oxidizing sites, probably consisting of lattice oxygen, O^{2-}.[9,10] Explanations of the role of each component in the catalytic action of such binary oxide systems as Cu–Sb,[14] Bi–Mo,[13,15] and others[16,17] appear to be based essentially on the same notion as that stated above, although the structure and generation of acidic and basic sites cannot be explained at present.

Let us now discuss the experimental results from this viewpoint. TiO_2–V_2O_5 (V/Ti=1/9) is rather basic, although it has a fair amount of acidic sites of weak acid strength. The addition of P_2O_5 to TiO_2–V_2O_5 gradually decreases the basicity and increases the acidity. Therefore, the ternary system containing a large amount of P_2O_5 is highly acidic but scarcely basic.

The oxidation activity for basic compounds, such as butadiene, is maximum at x=about 0.4 and is not correlated with the acidity of the catalyst, unlike MoO_3- or V_2O_5-based catalysts.[6,7,9,10] These results can be interpreted as follows. When the P_2O_5 content is low and the basic sites which are connected with the oxidizing sites, are sufficiently numerous, the oxidation activity is dependent mainly on the activation of the basic reactant (olefin) over the acidic sites. However, when, the P_2O_5 content is high and the oxidizing sites are strongly extinguished by the P_2O_5, the oxidation activity is then limited by the activation of oxygen but not by that of the reactant. It should be noted that the TiO_2–P_2O_5 system containing a large amount of P_2O_5 is inactive as an oxidation catalyst, due to the lack of oxidizing power, though it is highly acidic.[18] The same phenomenon was observed in the case of WO_3–P_2O_5–X_nO_m (X_nO_m=different metal oxides) catalysts, where the high oxidizing power of NiO, Co_3O_4, and MnO_2 is completely extinguished by WO_3–P_2O_5.[19]

On the other hand, in the case of the oxidation of an acidic compound, such as acetic acid, the activation of the reactant as well as of oxygen takes place on the basic sites, owing to the electron-donating ability to the electron-acceptor-type compounds, acetic acid and oxygen.[9,10] This view is consistent with the experimental results shown in Fig. 6.

As regards the selectivity, the results obtained from the TiO_2–V_2O_5–P_2O_5 system also support an earlier proposal that a requirement for an effective catalyst in "acid-formation" reactions is an acidic character and that a requirement for a catalyst to be effective in "base-formation" reactions is a moderate character both as an acid and a base.[1,6,7,9,10]

Conclusion

The character of the TiO_2–V_2O_5–P_2O_5 ternary catalysts can be modified from basic to acidic by controlling the P_2O_5 content.

The catalytic behavior of the TiO_2–V_2O_5–P_2O_5 system supports an earlier proposal that the activity and selectivity in mild oxidations can be interpreted in terms of the acid-base properties of the catalyst and the reactant. The acidic sites contribute to the activation of electron-donor-type reactants, while the basic sites are connected with the oxidizing sites and they also contribute to the activation of acidic reactants.

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