The Oxidation Activity and Acid-base Properties of V_2O_5-based Binary Catalysts

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(Received April 9, 1977)

The oxidation of *cis*-2-butene, butadiene, and acetic acid was carried out by using a series of V_2O_5–X_nO_m (atomic ratio=9: 1) catalysts with more than twenty metal oxides (X_nO_m). The results were compared with the dehydration activity for isopropyl alcohol (IPA), as a measure of acidity, and with the ratio, dehydrogenation activity for IPA/dehydration activity for IPA, used as a measure of the basicity of catalyst. The activity for the oxidation of butadiene and that for the isomerization of butene are correlated with the acidity, and the activity for the oxidation of acetic acid with the basicity of the catalyst. The selectivity to maleic anhydride from butene and butadiene is scarcely influenced by the introduction of metal oxides. Butene is mainly oxidized to acetic acid as a result of C–C fission. The selectivity to acetic acid is enhanced when the catalyst is highly acidic, decreasing with increase in basicity. It is concluded that the introduction of metal oxides into V_2O_5 modifies the acid-base properties of the catalyst, inducing a change in oxidation activity and selectivity.

Catalysts based on V_2O_5 have been used for a long time in the synthesis of sulfuric acid from sulfur dioxide and of carboxylic acids from aromatic hydrocarbons; they play an important part in the partial oxidation of organic substances. The characteristic feature of these catalysts is their effective specificity in "acid formation."

As a practical catalyst, pure V_2O_5 is rarely used. In most cases V_2O_5 is modified by combining it with oxides of other metals in order to enhance the catalytic action. Attempts have been made to determine the role of the additives as regards the structural,[1–6] electronic,[7–12] and other physico-chemical properties of the catalyst system.[4,13–16] It should be noted that the selectivity of acrolein to acrylic acid is connected with the electronegativity of the metal oxides used as second components added to V_2O_5 catalysts.[17]

The acid-base properties and their correlation with the oxidation activity and selectivity were studied in the case of many MoO_3 and V_2O_5-based binary catalysts, such as MoO_3–P_2O_5,[18] MoO_3–Bi_2O_3–P_2O_5,[19,20] MoO_3–V_2O_5,[21] MoO_3–TiO_2,[22] MoO_3–SnO_2,[23] MoO_3–Fe_2O_3,[24] V_2O_5–P_2O_5,[25] V_2O_5–TiO_2,[22] V_2O_5–SnO_2,[26] and V_2O_5–Fe_2O_3.[24] The catalytic activity for the oxidation of electron-donating (basic) reactants such as olefinic and aromatic hydrocarbons is correlated with the acidic nature of the catalyst surface, and that of acidic reactants such as carboxylic acids with the basic nature of the catalyst. The activity and selectivity in mild oxidations are governed by the acid-base properties of the catalyst and the reactant.[18–26]

The following two functions are required for a catalyst to be active in an oxidation reaction;

(1) activation of oxygen,

(2) activation of reactant molecules.

When a catalyst is potent in the activation of oxygen, *i.e.*, when it has high oxidizing power, the reaction takes place without requiring any activation of the reactant: it proceeds non-selectively toward CO_2 and H_2O. This is the case of deep oxidation.[27] On the other hand, when the oxidizing power of a catalyst is not very high, the reaction requires the activation of the reactant molecule as well as of oxygen. Thus the difference in the mode or degree of this reactant-activation brings about the selectivity of the 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;[28–30] the acidic sites contribute to the activation of the elctron-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 fact that V_2O_5 is a typical acidic oxide leads us to the prediction that the addition of metal oxide to V_2O_5 modifies the acid-base properties of the catalyst system, and that this modification, in turn, induces a change in the catalytic behavior.

In the present work, we have attempted to confirm how the addition of a small amount of metal oxide to V_2O_5 modifies the acid-base properties as well as the oxidation activity and selectivity and to find the correlation between the acid-base properties and catalytic behavior.

Experimental

Catalysts. The catalysts used in this study were a series of V_2O_5-based binary oxides, V_2O_5–X_nO_m. As the second component, X_nO_m, more than twenty metal oxides, including almost all those used in practice, were tested. As starting materials, we used nitrates for Al, Sb, Bi, Te, Fe, Ni, Cr, Co, and Zn, ammonium salts of oxo-acid for V, Mo, and W, chlorides (converted into hydroxides with dilute ammonia) for Sn and Ti, hydrates for Ca, Mg, and K, acetate for U, H_2SO_4 for S, and H_3PO_4 for P. The surface area of these catalysts were determined by the BET method, using nitrogen at −196 °C.

Determination of Acidic and Basic Properties. Since the V_2O_5-based mixed oxides are colored and small in surface area, it is not easy to determine their acidity and basicity by the ordinary titration method[31,32] or by studying the adsorption of a basic or acidic molecule in the gas phase. However, from a comparison of the catalytic activities for isopropyl alcohol (IPA) with the acidity-basicity data directly measured on many kinds of mixed catalysts, such as MoO_3–Bi_2O_3–P_2O_5,[20] MoO_3–TiO_2,[22] MoO_3–SnO_2,[23] MoO_3–Fe_2O_3,[24] V_2O_5–TiO_2,[22] V_2O_5–SnO_2,[26] V_2O_5–Fe_2O_3,[24] and TiO_2–

X_nO_m (X_nO_m=various kinds of metal oxides),[33] it has been found that the activity for the dehydration of IPA to propylene (r_p) represents the acidity of the catalyst and that the value of the r_a/r_p ratio, where r_a is the activity for the dehydrogenation of IPA to acetone, is also valid as an index of basicity;

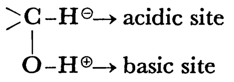
$$\text{acidity} \propto \text{dehydration rate} \tag{1}$$

$$\text{basicity} \propto \frac{\text{dehydrogenation rate}}{\text{dehydration rate}}. \tag{2}$$

The results indicate that acidic and basic sites take part almost equally in the dehydrogenation of IPA;

$$\text{dehydrogenation rate} \propto (\text{acidity})(\text{basicity}). \tag{3}$$

This reaction may proceed by means of a concerted mechanism, *e.g.*,[34)]



$$\begin{array}{l} >\text{C-H}^{\ominus}\rightarrow \text{acidic site}\\ \;\;| \\ \text{O-H}^{\oplus}\rightarrow \text{basic site}\end{array}$$

Thus we used the values of r_p and r_a/r_p as measures of the acidity and basicity, respectively, of the catalysts.

Catalytic Activity Measurements. The vapor-phase oxidation of *cis*-2-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 concentrations of butene, butadiene, acetic acid, and IPA were 0.67, 0.67, 1.5, and 1.65 mol%, in the air; the total flow rate (at 25 °C) was kept constant at 1.5 l/min, the amout of catalyst used being 2—30 g. The reactor and experimental procedures were the same as those employed in previous works.[18–26)]

Results and Discussion

Acidic and Basic Properties. A gaseous mixture of IPA with air was passed through a bed of the catalyst (2—6 g) held at 175 °C. The rates of dehydration (r_p) and dehydrogenation (r_a) [mol/h g-cat], which are known to be almost of zero-order with respect to the IPA concentration,[18–26)] were obtained for each catalyst.

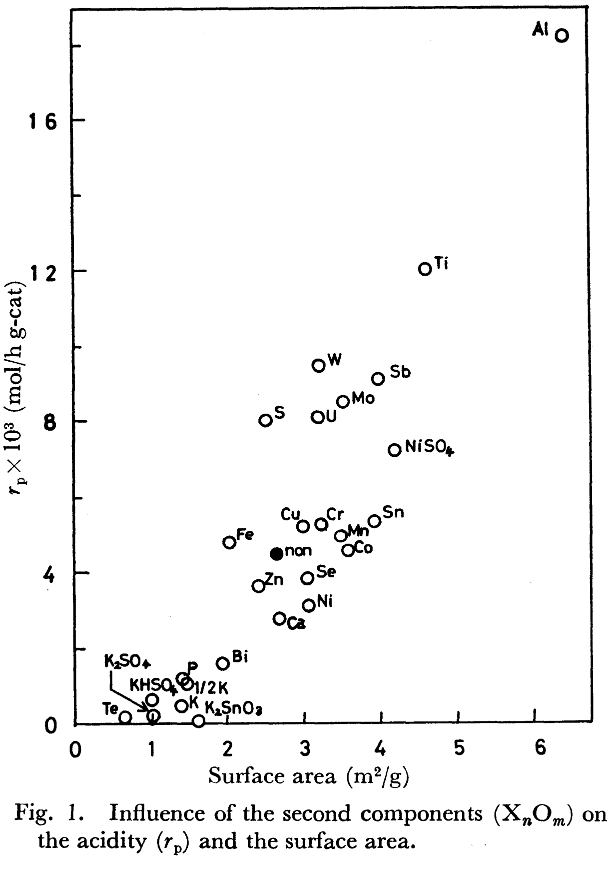


Fig. 1. Influence of the second components (X_nO_m) on the acidity (r_p) and the surface area.

The values of r_p together with the surface areas, S (m²/g) are given in Fig. 1. Introduction of the additives (X_nO_m) causes a remarkable change both in the surface area and the specific acidity (r_p/S) of the catalyst. It should be noted that introduction of TeO_2, K_2SnO_3, and K_2SO_4 into V_2O_5 decreases the acidic property significantly.

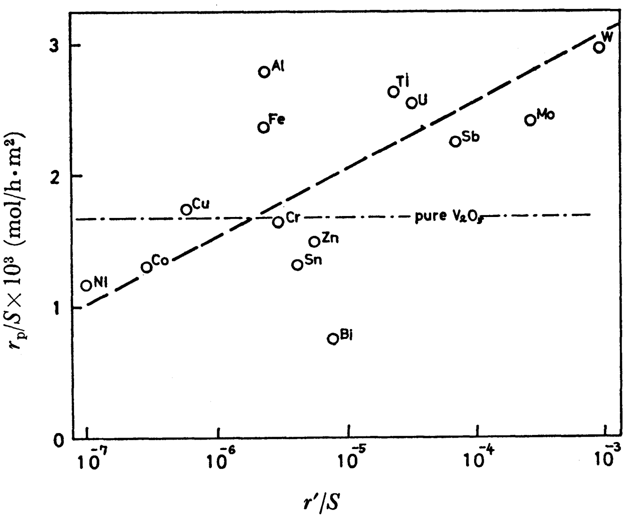


Fig. 2. The specific acidity of the binary system (V_2O_5–X_nO_m), r_p/S, as a function of that of the second component (X_nO_m) alone, r'_p/S.
r_p: The dehydration rate at 175 °C,
r'_p: the dehydration rate at 190 °C.

In Fig. 2 the specific acidity of the binary system, r_p/S, is plotted as a function of that of the second component (X_nO_m) alone, r'_p/S, obtained previously.[35)] A rough correlation holds between r_p/S and r'_p/S, though a disparity and some exceptions are found. Addition of such acidic elements as P_2O_5 and TeO_2 decreases the acidity.

Figure 3 shows the relationship between the specific acidity, r_p/S, and the basicity, r_a/r_p. The basicity decreases a great deal with an increase in acidity, as might be expected in the case of a liquid acid-base, except for the cases of P_2O_5 and TeO_2. Introduction of P_2O_5 decreases both the acidity and the basicity.

Isomerization Activity for Butene. The oxidation of butene over a V_2O_5-based catalyst is always accompanied by its isomerization. The influence of the additives on the activity for the isomerization of butene was studied. The experiments were carried out at the *cis*-2-butene concentration of 0.67 mol % in the air, at a total flow rate of 1.5 l/min, and at 220 °C, the catalyst amount being varied in the 2.5—30 g range. The ratio of (*trans*-2-butene + 1-butene)/(*cis*-2-butene + *trans*-2-butene + 1-butene) corresponding to the surface area of 5 m², I, which is far from the thermodynamic equilibrium (I_e) of *ca.* 0.65, was adopted as a measure of the specific activity for isomerization. The data are plotted against the value of r_p/S in Fig. 4.

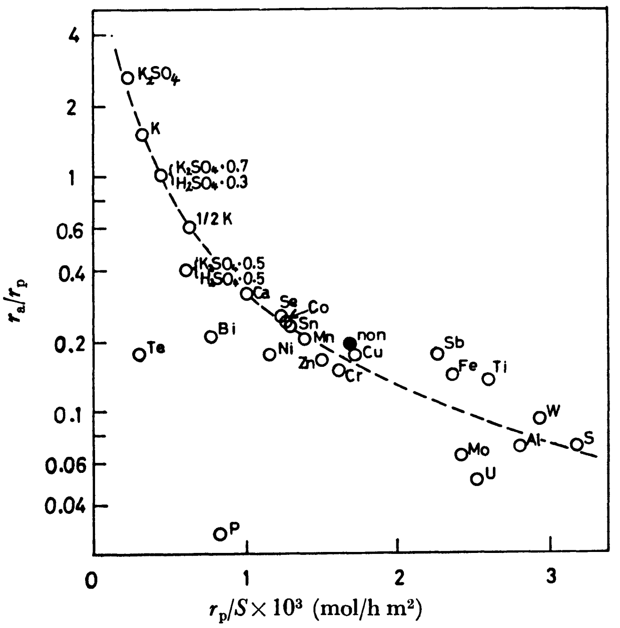


Fig. 3. Relation between the acidity (r_p/S) and the basicity (r_a/r_p).

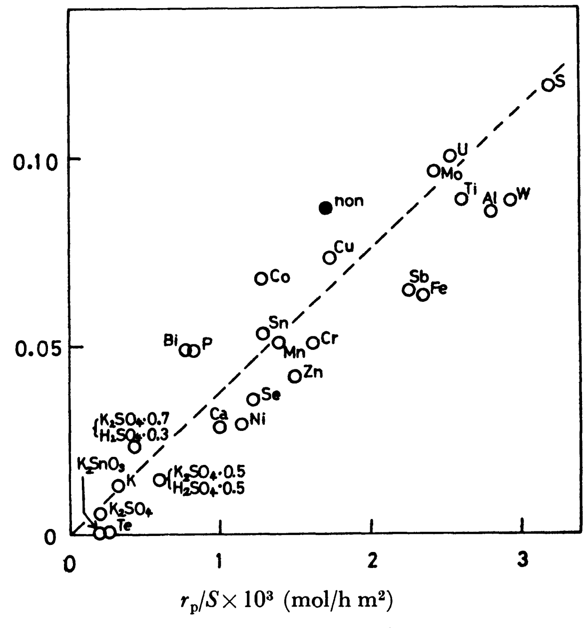


Fig. 4. The isomerization activity (I) against the acidity (r_p/S.)

A linear relationship is obtained between isomerization activity and acidity of the catalyst. This indicates[22,23,26] that, under the circumstances of the oxidation reaction in a flow system, the isomerization is catalyzed only by the acidic sites, and that the basic sites which can also catalyze the isomerization in the absence of oxygen in a closed[36] or pulse-reaction system[37] are poisoned by CO_2 or other acidic products.

Oxidation Activity for Olefin. The promotive effect of the additives on the oxidation activity for such basic reactants as olefins was also examined. The oxidation of 1,3-butadiene was chosen as a model reaction for convenience of experimental procedure. It was carried out over a seires of V_2O_5-X_nO_m catalysts at 285 °C, the amount of the catalyst being varied from 2.5 to 25 g. The initial rate of butadiene disappearance, r_B (mol/h g-cat), was adopted as a measure of activity. The specific activity, r_B/S, is plotted as a function of the specific acidity, r_p/S, in Fig. 5.

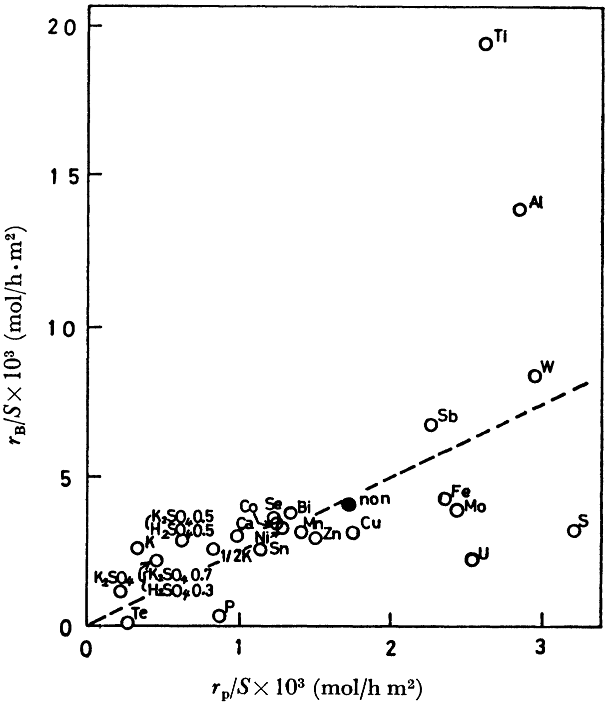


Fig. 5. The oxidation activity for butadiene (r_B/S) as a function of the acidity (r_p/S).

A moderately good correlation is obtained between oxidation activity and acidity, except for several oxides such as TiO_2, Al_2O_3, P_2O_5, SO_3, and U_3O_8. The data are in line with the results obtained previously,[18-26] indicating that the acidic sites play an important role in catalyzing the oxidation of olefin. It seems that the large deviation of V_2O_5-TiO_2 and V_2O_5-Al_2O_3 is connected to their large surface area. When the oxidation activity per unit volume of catalyst is very high, the evolution of heat per unit volume of catalyst becomes great and, the real temperature of the catalyst surface becomes much higher than the measured temperature, which gives rise to a large increase in apparent activity. The disparity of these results may arise in part from the participation of another factor in the catalysis; *e.g.*, the activation of oxygen which seems to be associated with (1) the strength of metal-oxygen bonding and (2) the possibility of incorporation of gaseous oxygen into the crystal lattice oxygen by electron donation from the catalyst.

Oxidation Activity for Acid. The influence of the additives on the oxidation activity for acidic compounds was also examined. Acetic acid was chosen as the reactant. The initial rate of oxidation to CO_2 at 325 °C, r_A (mol/h g-cat), was adopted as a measure of activity.

The specific activity, r_A/S, is plotted as a function of the basicity, r_a/r_p, in Fig. 6. The basic sites of the catalyst are considered to contribute to the activation of acidic compounds.[19-22,24]

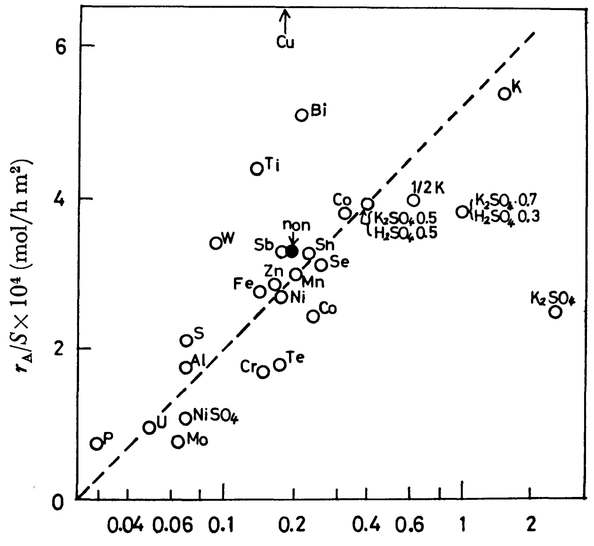


Fig. 6. The oxidation activity for acetic acid (r_A/S) as a function of the basicity (r_a/r_p).

A relatively good correlation is found between r_A/S and r_a/r_p. This supports the validity of the above conception that the basic sites of catalysts contribute to the activation of an acidic compound and oxygen (electron-accepting compound). The large deviation of CuO and K_2SO_4 is supposed to be caused by the strength of metal-oxygen bonding.

Selectivity in Oxidation. The effect of additives on selectivity in the oxidation of olefins was examined. Butadiene was oxidized in the presence of excess air (butadiene=0.67 mol %) over the series of V_2O_5–X_nO_m catalysts with a variety of second components, X_nO_m. At a high conversion of *ca.* 80—95%, the main product, besides CO_2 and CO, was maleic anhydride as in earlier results. The amount of acetic acid was fairly small.

The selectivity of butadiene to maleic anhydride at a conversion of 80—90% is plotted as a function of the basicity of the catalyst, r_a/r_p, in Fig. 7. The selectivity is *ca.* 50 mol % and nearly independent of the additives, except in the cases of K_2SO_4 and K_2SnO_3 where the oxidation activity is extremely low. Since V_2O_5-based catalysts are acidic enough, *viz.*, they are inactive for acidic compounds, the selectivity is not limited by the consecutive decomposition of the maleic anhydride produced, but by the selectivity in the steps from butadiene to maleic anhydride.

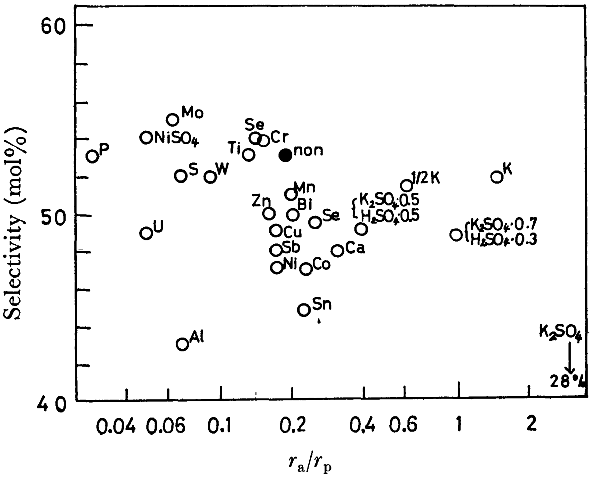


Fig. 7. The selectivity from butadiene to maleic anhydride at a conversion of 80—95% as a function of the basicity of the catalyst (r_a/r_p).

The selectivity in the oxidation of *cis*-2-butene was examined. The formation of butadiene was very low, even at low oxygen concentrations. The butadiene produced can be oxidized more rapidly than butene, since the catalysts are acidic and butadiene is more basic than butene.[19,20,22,26)]

Concerning maleic anhydride formation, the selectivity from butene is fairly small as compared with that from butadiene. A significant amount of acetic acid is formed at the expense of maleic anhydride as has been reported by Brockhaus.[38)] The selectivities to maleic anhydride and acetic acid at a 80—95% conversion are plotted as a function of the basicity of the catalyst, r_a/r_p, in Fig. 8.

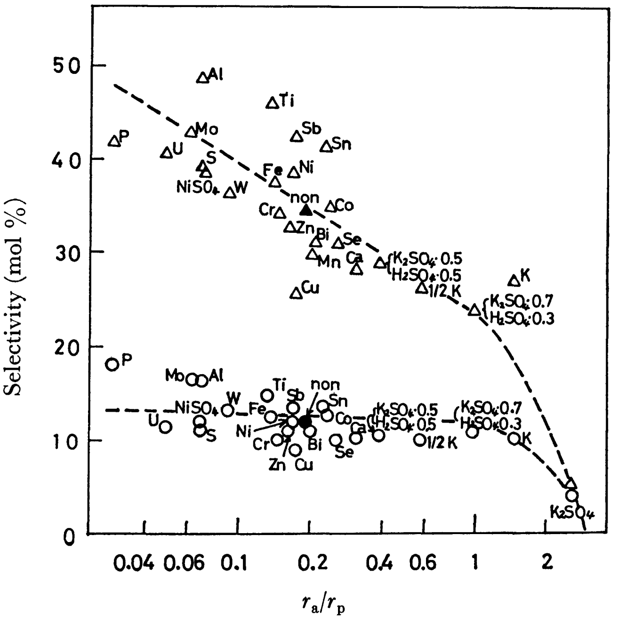


Fig. 8. The selectivity from *cis*-2-butene to maleic anhydride and acetic acid at a conversion of 80—95% as a function of the basicity (r_a/r_p).

○ =Maleic anhydride, △ =acetic acid + maleic anhydride.

The selectivity to maleic anhydride is *ca.* 12 mol % for each catalyst, while selectivity to acetic acid decreases with an increase in the basicity, r_a/r_p. The results in Fig. 8, which coincide with the data of the oxidation activity for acetic acid (Fig. 6), reveal that acetic acid is decomposed more easily than maleic anhydride by means of the basic sites of the catalyst. It is of interest that, in contrast to butadiene, butene is mainly oxidized to acetic acid.

The selectivity to maleic anhydride over V_2O_5-based catalysts not containing a large amount of P_2O_5 is mainly limilted by the selectivity at the step of allylic oxidation, butene→butadiene.[39] This is because butene is more susceptible to the C–C fission than to the allylic C–H fission.

Thus it can be said that the V_2O_5-based catalysts, if they are highly acidic and moderately basic, are effective for the oxidation of butene to acetic acid.

Conclusion

The introduction of a small amount (10 atom %) of metal oxides into a V_2O_5 catalyst causes a remarkable change in the surface area and the acid-base properties.

The acidity of the binary system, V_2O_5–X_nO_m (9: 1), is roughly correlated to that of the second component, X_nO_m, itself, though there are many exceptions. In general the basicity decreases markedly with acidity.

The activity for the isomerization of 1-butene is proportional to the acidity of catalyst. The oxidation activity for olefin is roughly correlated with the acidity and that for acid is correlated with the basicity of the catalyst.

Since the V_2O_5–X_nO_m (9: 1) catalysts are rather acidic, the selectivity of butadiene to maleic anhydride, which is relatively stable, is *ca.* 50 mol % and is scarcely influenced by the introduction of any metal oxides except for $X_nO_m=K_2SO_4$ and K_2SnO_3. Over these V_2O_5–X_nO_m catalysts, butene is mainly oxidized to acetic acid as a result of the C–C fission which takes place in preference to the allylic C–H fission, little butadiene being formed from butene. The selectivity to acetic acid decreases with an increase in the basicity of the catalyst, since acetic acid is decomposed easily with the basic sites.

This agrees with the results of our earlier works and leads us to conclude that the introduction of metal oxides into V_2O_5 modifies the acid-base properties of the catalysts, and that this modification induces the main change in oxidation activity and selectivity.

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