

Partial Oxidation of Propylene on V_2O_5 - P_2O_5 -Based Catalysts

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The vapor-phase oxidation of propylene was studied over V_2O_5 , V_2O_5 - P_2O_5 , and V_2O_5 - P_2O_5 - TeO_2 catalysts in the presence of water vapor. On pure V_2O_5 , the oxidation products were acetic acid and carbon oxides, plus a small amount of acetone. As the content of phosphorus added to V_2O_5 increases, the oxidation activity markedly decreases; on the other hand, the selectivity to acrylic acid increases and passes through a maximum at P/V atomic ratio = 1.15 to 1.6, while that to acetic acid gradually decreases. With the V_2O_5 - P_2O_5 (P/V = 1.15) catalyst, the yield of acrylic acid attains 25 mol%, that of acetic acid is less than 10 mol%, and that of acrolein is less than 0.7 mol%. The effects of the third components added to V_2O_5 - P_2O_5 (P/V = 1.15) were also studied. It was found that TeO_2 is the sole additive which can improve the catalyst performance. As the amount of TeO_2 increases, the specific oxidation activity increases, as do the formation of acrolein and the sum of the yields of acrylic acid and acrolein, while the formation of acetic acid passes through a maximum at Te/V = 0.02 to 0.04. With the V_2O_5 - P_2O_5 - TeO_2 (Te/P/V = 0.15/1.15/1) catalyst, the yield of acrylic acid attains 38 mol% when air is used as the oxidant and 42 mol% when oxygen is so used. The effects of reaction variables, such as the oxygen concentration, the propylene concentration, the water vapor, and the temperature, on the activity and selectivity were also studied. © 1986 Academic Press, Inc.

INTRODUCTION

It is well known that propylene is oxidized quite selectively to acrolein over Bi_2O_3 - MoO_3 , U_3O_8 - Sb_2O_5 , SnO_2 - Sb_2O_5 , and Fe_2O_3 - Sb_2O_5 catalysts. Indeed, a great number of studies have been made of this reaction (1-7). In addition, propylene is oxidized directly to acrylic acid over MoO_3 -based mixed oxides such as Co_3O_4 - MoO_3 (3, 4, 6). On the other hand, it is known that propylene is oxidized to acetone in the presence of water vapor over some MoO_3 -based oxides, above all, SnO_2 - MoO_3 (8). In contrast to these findings, it has been reported (9) that propylene is oxidized mainly to carbon oxides over V_2O_5 and V_2O_5 -based mixed oxide catalysts. This may be the reason why few studies has been done on the oxidation of propylene with V_2O_5 -based oxides.

V_2O_5 - P_2O_5 catalysts exhibit an excellent performance in the oxidation of *n*-butane

and *n*-butene to maleic anhydride. It has been proposed (10) that the phosphorus plays a role in depressing a side reaction, e.g., the hydration of butene to 2-butanol, which is further oxidized to acetic acid via methyl ethyl ketone (11). In line with this thought, it can be predicted that the addition of phosphorus to V_2O_5 induces a decrease in the hydration, which directs the propylene to the formation of acetic acid and carbon oxides via acetone, and that, as a result, it directs the propylene to allylic oxidation.

On the other hand, V_2O_5 -based oxides are known to be effective as catalysts for the oxidation of acrolein to acrylic acid (3, 12, 13). Therefore, propylene can be expected to be oxidized directly to acrylic acid over V_2O_5 - P_2O_5 catalysts.

In this study, we focused our attention on the oxidation of propylene with V_2O_5 and V_2O_5 - P_2O_5 -based oxide catalysts and attempted to clarify the effects of catalysts

and reaction variables, since no detailed information about this oxidation reaction has yet been reported.

EXPERIMENTAL

Catalysts

V₂O₅ catalyst. V₂O₅ powder was partially dissolved in water by using oxalic acid. The mixture was evaporated with stirring. The obtained paste was then dried in an oven at 150°C for 5 h.

V₂O₅-P₂O₅ (P/V atomic ratio = 0.9) catalyst. This catalyst was prepared according to a patent (14); that is, V₂O₅ was dissolved in tetrahydrofuran by slowly adding the required quantities of POCl₃. Then, the tetrahydrofuran was removed by distillation under reduced pressure. The paste thus obtained was dried in an oven at 150°C for 6 h.

V₂O₅-P₂O₅ (P/V > 1.0) catalysts. These catalysts were also prepared according to a patent (15); that is, V₂O₅ was reduced by refluxing it in a solution consisting of benzyl and isobutyl alcohols for 2 h; a black suspended precipitate was thus formed. Then, the required quantities of 98% H₃PO₄ were added to the solution, and the solution was refluxed again for 2 h; a light blue, suspended precipitate was thus obtained. The solvent was removed by distillation. The paste thus obtained was dried in an oven at 150°C for 6 h.

V₂O₅-P₂O₅-M_nO_m catalysts. Fine powder of the above-mentioned precursor of the V₂O₅-P₂O₅ (P/V = 1.15) catalyst was added to an aqueous solution containing the required amounts of the third metallic compounds, such as Cs₂CO₃, Li₂CO₃, Bi(NO₃)₃, Co(NO₃)₂, (CH₃COCHCOCH₃)₂ TiO, ZrOCl₂, H₃BO₃, Sb₂O₃, H₆TeO₆, and H₃PMo₁₂O₄₀. The mixture was kneaded to achieve a complete mixing. The paste thus obtained was dried in an oven at 150°C for 6 h.

In each of the above procedures, the recovered catalyst precursor was first calcined at 300°C for 6 h in a stream of air

flowing at a rate of 2.0 vol/vol/min, then it was broken up and sieved to a 10–20 mesh size. Finally, it was calcined again at 450°C for 12 h in a stream of air, flowing at a rate of 1.0 vol/vol/min.

Oxidation Procedures

The oxidation of propylene was conducted in a continuous-flow reaction system. The reactor was made of a steel tube, 50 cm long and 1.8 cm i.d., mounted vertically and immersed in a lead bath. Air or oxygen–nitrogen mixture was fed in from the top of the reactor, with water being introduced by means of a micro liquid-feeder. Unless otherwise indicated, the reaction conditions were fixed as follows; propylene concentration, 2.5 vol% in air; water vapor concentration, 16.2 vol% in air; sum of the flow rates of air plus propylene, 400 ml (at 20°C)/min (ca. 1.0 mol.h); amount of catalyst used, 10 g.

The effluent gas from the reactor was led into three chilled water-scrubbers to recover the water-soluble compounds. At the end of 1 h, the content of the water-scrubbers was collected (120 ml). The reaction products were analyzed by gas chromatographs; a 1-m column of molecular sieve 13× for CO; a 6-m column of propylene carbonate for CO₂ and propylene; a 2-m column of PEG 20M at 100°C for aldehydes, ketones, and alcohols; a 1-m column of SP-1200 + H₃PO₄ at 130°C for acids. The amount of total acid was also analyzed by titration with 0.10 N NaOH using a pH meter.

The yield and selectivity for a particular product were defined as mole percentage yield and selectivity on a carbon-accounted-for basis.

RESULTS

Performance of the V₂O₅ Catalyst

The oxidation of propylene was conducted with the pure V₂O₅ catalyst under the conditions described in the Experimental section, except that the amount of catalyst used was 5.0 g. The products were ace-

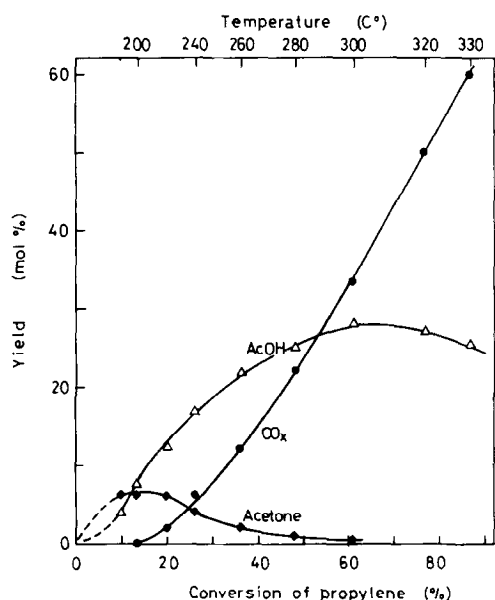


Fig. 1. Oxidation of propylene on the pure V_2O_5 catalyst. (Δ) Acetic acid, (\bullet) acetone, (\bullet) carbon oxides.

tic acid and carbon oxides, plus a small amount of acetone. Formaldehyde was also obtained, but only at low temperatures below 180°C . The change in the yields of each product with the extent of the reaction was studied by elevating the reaction temperature from 180 to 330°C (Fig. 1).

Performance of the V_2O_5 - P_2O_5 ($P/V = 1.15$) Catalyst

Figure 2 shows the results obtained with the V_2O_5 - P_2O_5 ($P/V = 1.15$) catalyst. The profile of the product distributions is completely different from that obtained in the case of the pure V_2O_5 (Fig. 1). The main partial oxidation product is acrylic acid, and the yield attains $25\text{ mol}\%$, while the yield of acetic acid is less than $10\text{ mol}\%$. The formation of acrolein is observed, but the yield is less than $0.7\text{ mol}\%$.

Effect of the P/V Composition

As may be seen in Figs. 1 and 2, there exists a large difference in the catalyst performances between the pure V_2O_5 and V_2O_5 - P_2O_5 catalysts. Therefore, the effect

of the P/V composition on the catalytic action was studied. As the index of the oxidation activity, the temperature required for the propylene conversion of 50% with a fixed level (50 m^2) of the catalyst surface area, t_{50} ($^\circ\text{C}$), was employed, because the range of activity variation was so wide that it is hard to express it by a reaction rate at a fixed temperature. The results are shown, together with the surface area of the catalysts, in Fig. 3. The activity markedly decreases with the increase in the phosphorus content.

The effect of the addition of phosphorus on the yield of acrylic acid was then studied. As may be seen in Fig. 4, the selectivity to acrylic acid (the slope of the curve) increases with the phosphorus content, passes through a broad maximum at $P/V = 1.15$ to 1.6 , and then decreases with a further increase in the phosphorus content.

The change in the yield of acetic acid is shown in Fig. 5. In the cases of all the catalysts, the yield attains a maximum value at a propylene conversion from 50 to 60% . However, it is clear that the formation of

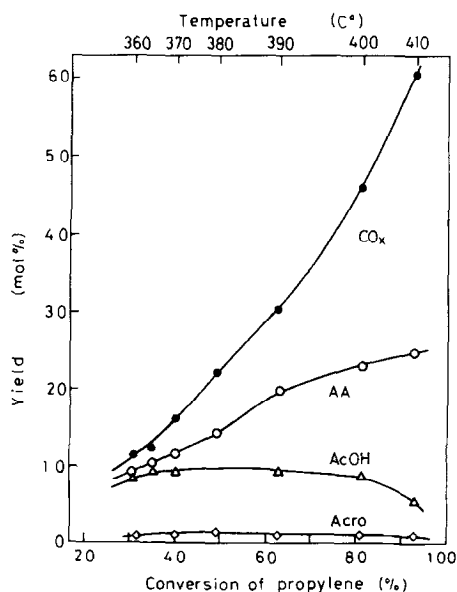


Fig. 2. Oxidation of propylene on the $P/V = 1.15$ catalyst. (\circ) Acrylic acid, (Δ) acetic acid, (\diamond) acrolein, (\bullet) carbon oxides.

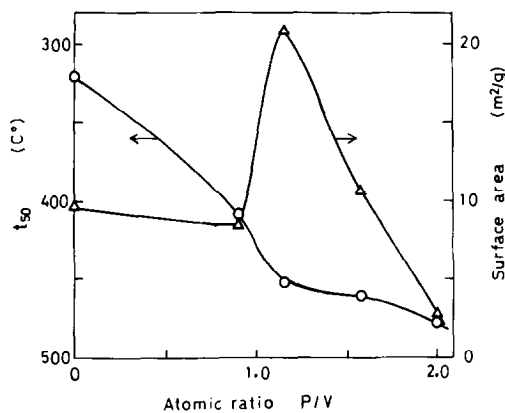


FIG. 3. Effect of the P/V composition on the catalytic activity and the surface area.

acetic acid decreases with an increase in the phosphorus content.

Effect of the Third Component Added to $V_2O_5-P_2O_5$

In order to improve the yield of acrylic acid, attention was given to the modification of the $V_2O_5-P_2O_5$ (P/V = 1.15) catalyst by adding various kinds of third metallic compounds, such as Cs_2O , Li_2O , Bi_2O_3 , Co_3O_4 , TiO_2 , ZrO_2 , B_2O_3 , Sb_2O_3 , TeO_2 , and MoO_3 . The amount of the third metallic ions (M) was fixed: M/V atomic ratio = 1/10. A series of catalysts were tested for the

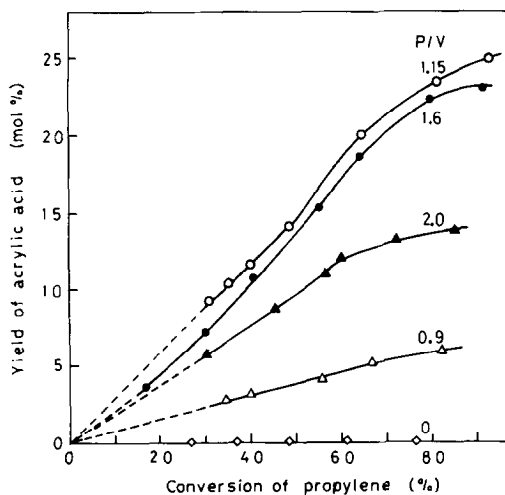


FIG. 4. Effect of the P/V composition on the yield of acrylic acid.

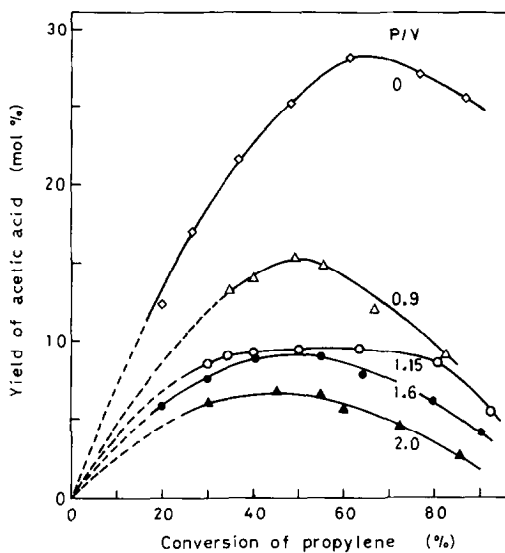


FIG. 5. Effect of the P/V composition on the yield of acetic acid.

ability to form acrylic acid. It was found that only TeO_2 shows an improved performance; none of the others is effective.

Figure 6 shows the performance obtained

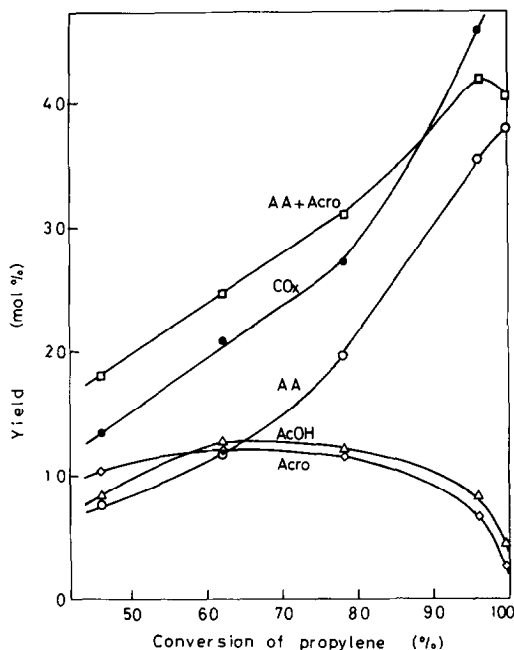


FIG. 6. Oxidation of propylene on the $Te/P/V = 0.15/1.15/1$ catalyst. (○) Acrylic acid, (◇) acrolein, (△) acetic acid, (●) carbon oxides, (□) acrylic acid plus acrolein.

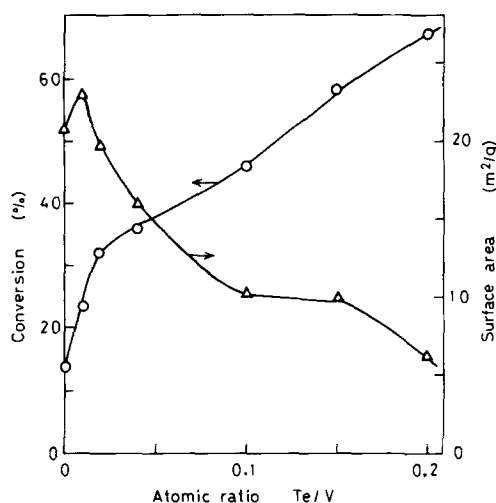


FIG. 7. Effect of the amount of TeO_2 added to $P/V = 1.15$ oxide on the catalytic activity and the surface area.

with the V_2O_5 - P_2O_5 - TeO_2 ($Te/P/V = 0.15/1.15/1$) catalyst. The selectivity to acrylic acid (the slope of the curve) increases steadily with an increase in the extent of reaction up to the propylene conversion of 99%. The yield of acrylic acid attains 38

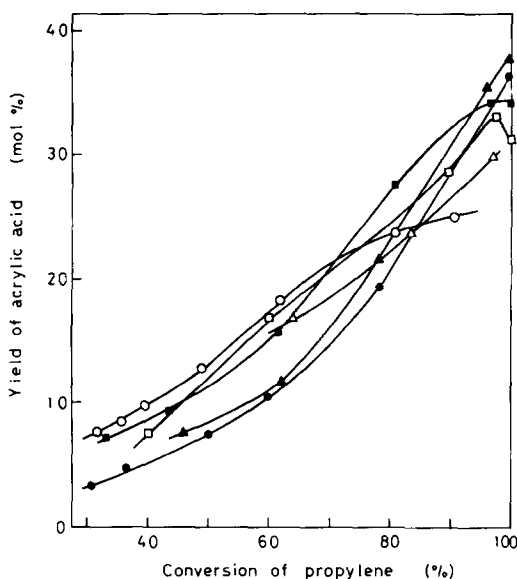


FIG. 8. Effect of the amount of TeO_2 added to $P/V = 1.15$ oxide on the yield of acrylic acid. Te/V composition; (○) 0, (△) 0.02, (□) 0.04, (●) 0.10, (▲) 0.15, (■) 0.20.

mol%, while that of the sum of partial oxidation products, i.e., acrylic acid, acetic acid, and acrolein, attains 51 mol%.

Effect of the Amount of TeO_2 Added to V_2O_5 - P_2O_5

The effect of the amount of TeO_2 added to V_2O_5 - P_2O_5 ($P/V = 1.15$) on the catalytic action was studied. As the index of the oxidation activity, the conversion of propylene with a fixed level (10 m^2) of the catalyst surface area and at 350°C was employed. The results are shown, together with the surface area of the catalysts, in Fig. 7. The specific activity increases with the TeO_2 content up to $Te/V = 0.02$ and it increases less steeply with a further increase in the TeO_2 content. The surface area of catalyst decreases with the TeO_2 content at $Te/V > 0.01$.

The effect on the formation of acrylic acid, acrolein, and acetic acid is shown in Figs. 8, 9, 10, and 11.

Figure 9 indicates that the formation of acrolein is very small when the content of TeO_2 is small, $Te/V < 0.04$, while it markedly increases when the TeO_2 content is higher, $Te/V > 0.10$, and that it shows a maximum value at the propylene conversion of about 60%.

As may be seen in Fig. 10, the sum of the yields of acrylic acid and acrolein increases almost linearly with the extent of reaction,

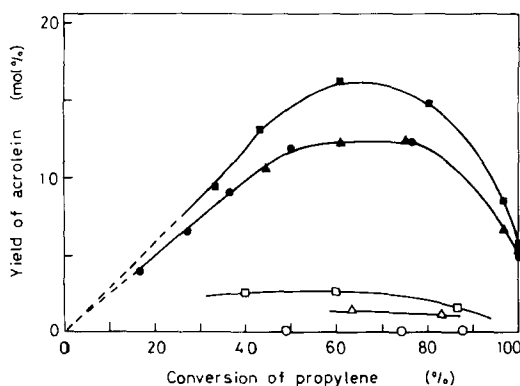


FIG. 9. Effect of the amount of TeO_2 added to $P/V = 1.15$ oxide on the yield of acrolein. Te/V composition; (○) 0, (△) 0.02, (□) 0.04, (●) 0.10, (▲) 0.15, (■) 0.20.

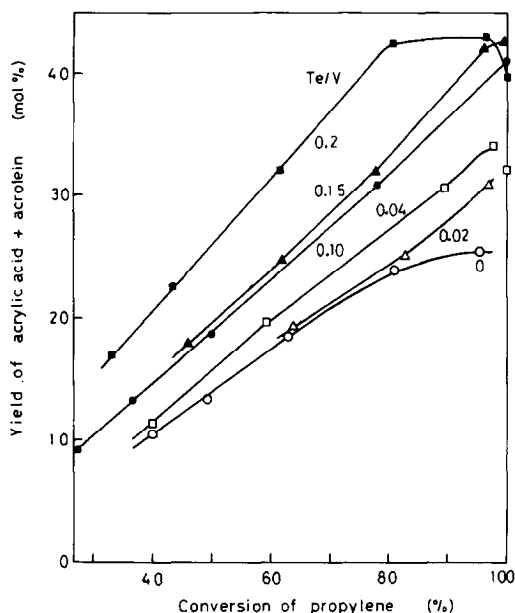


FIG. 10. Effect of the amount of TeO_2 added to $\text{P/V} = 1.15$ oxide on the yield of acrylic acid plus acrolein. Symbols are the same as for Fig. 8.

and it increases steadily with the increase in the TeO_2 content.

Figure 11 indicates that the yield of acetic acid shows a maximum value at the propylene conversion of from 50 to 80%, and that the formation of acetic acid markedly increases with the addition of a small amount of TeO_2 and passes through a maximum at

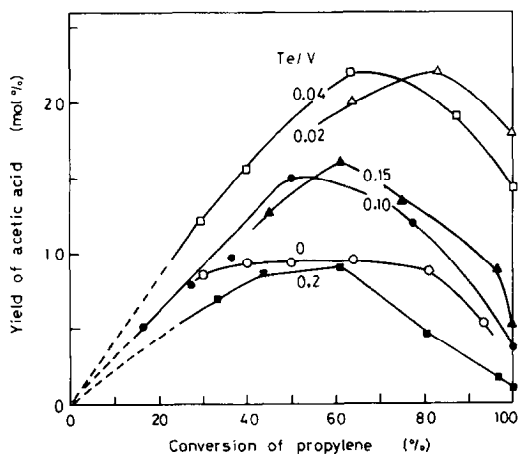


FIG. 11. Effect of the amount of TeO_2 added to $\text{P/V} = 1.15$ oxide on the yield of acetic acid. Symbols are the same as for Fig. 8.

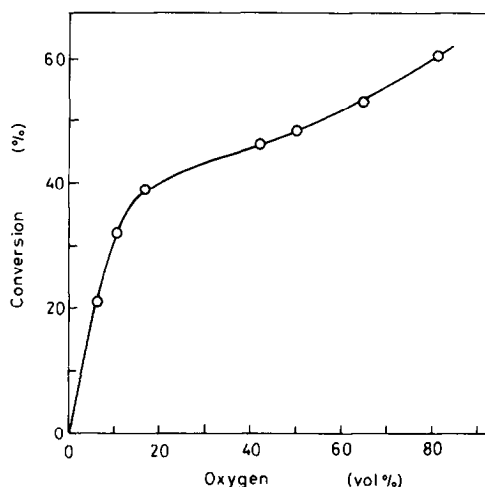


FIG. 12. Effect of the concentration of oxygen on the conversion of propylene.

$\text{Te/V} = 0.02$ to 0.04 . Then it decreases with a further increase in the TeO_2 content.

Effects of Reaction Variables

Oxygen concentration. The reaction was conducted with the $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5\text{-TeO}_2$ ($\text{Te/P/V} = 0.15/1.15/1$) catalyst by changing the initial concentration of oxygen from 6.3 to 81.3 vol%, while fixing the other conditions as described in the Experimental section. The change in the propylene conversion at 360°C is shown in Fig. 12. The conversion increases almost proportionally to the oxygen concentration at the concentration below 16 vol%, but it increases less steeply with a further increase in the oxygen concentration.

Figure 13 shows the results obtained by using oxygen as the oxidant in the temperature range from 320 to 360°C . Comparison of these results with those obtained by using air as the oxidant (Fig. 6) reveals that, as the oxygen concentration increases, the formation of acrylic acid increases at the expense of a decrease in the formation of acrolein, while the formation of acetic acid remains almost unchanged.

Propylene concentration. The reaction was conducted by changing the initial concentration of propylene from 1.0 to 7.8

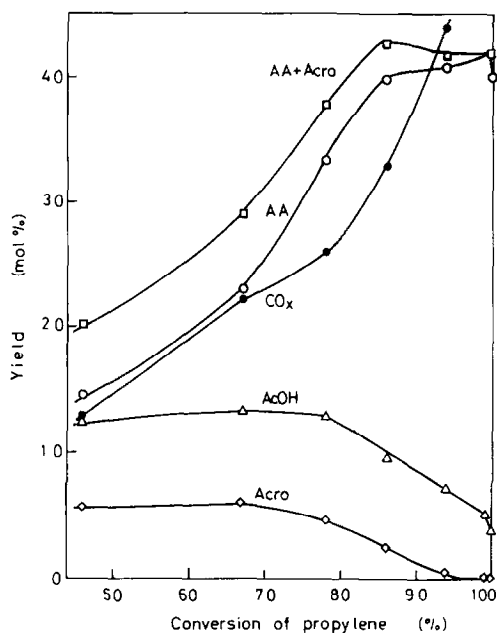


Fig. 13. Oxidation of propylene using oxygen as the oxidant. Feed composition; $C_3H_6-H_2O-O_2 = 2.5-16.2-81.3$ vol%. Symbols are the same as for Fig. 6.

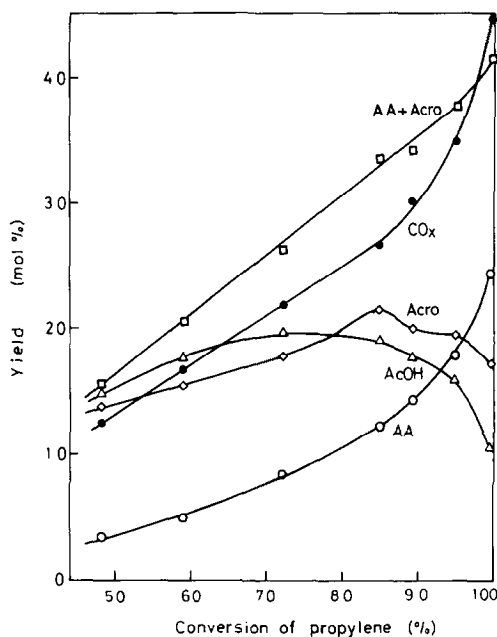


Fig. 14. Oxidation of propylene with a high propylene concentration. Feed composition; $C_3H_6-H_2O-air = 7.8-16.2-76.0$ vol%. Symbols are the same as for Fig. 6.

vol% in air. The rate increased to a certain extent with the increase in the propylene concentration when the concentration was less than 2.5 vol%, but it ceased to increase with a further increase in the oxygen concentration.

Figure 14 shows the results obtained with the propylene concentration of 7.8 vol% in air. Comparison of these results with those obtained with the propylene concentration of 2.5 vol% in air (Fig. 6) reveals that, as the propylene concentration increases, the formation of both acrolein and acetic acid increases at the expense of a decrease in the formation of acrylic acid.

Water vapor. With the addition of water vapor into the feed gas in the range from zero to 61 vol%, the rate of reaction remains almost unchanged. In order to clarify the effect of water vapor, another series of experiments were conducted with a propylene concentration of 5.0 vol% in air. The selectivities to each product at a fixed level (98%) of the propylene conversion are plotted as a function of the water vapor concen-

tration in Fig. 15. As the water vapor concentration increases, the selectivity to acrylic acid and acetic acid increases, while that to acrolein decreases.

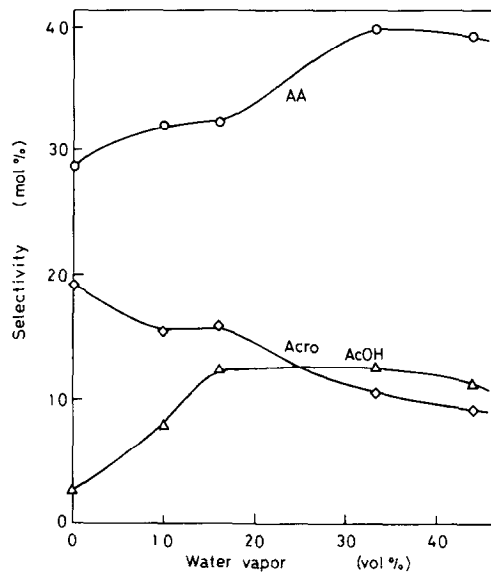
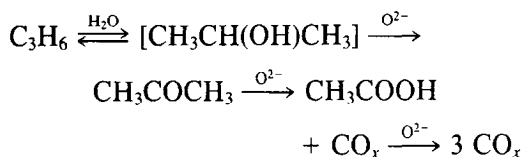


Fig. 15. Effect of the concentration of water vapor on the product distribution. Symbols are the same as for Fig. 6.

Reaction temperature. The effect of the reaction temperature on the product distribution was studied by comparing the yields obtained at a fixed level (90%) of the propylene conversion because the product distribution is dependent on the extent of reaction; the results were obtained by changing the amounts of catalyst used from 0.7 to 10 g. Figure 16 shows the results obtained by using oxygen as the oxidant. It was found that as the elevation of temperature, the formation of acrolein increases, while that of acrylic acid and acetic acid decreases.

DISCUSSION

The results represented in Fig. 1 reveal that, on the pure V_2O_5 catalyst, the oxidation of propylene proceeds mainly through the following series of consecutive steps:



The first step is a hydration of the propylene catalyzed by the action of acidic sites; the second step is an oxidative dehydrogenation of 2-propanol, which is catalyzed mainly by the action of basic sites, and the third and fourth steps consist of oxidative C—C fission. The equilibrium concentration of 2-propanol is very low under the present reaction conditions (16); therefore, the rate of propylene consumption is dependent on the catalytic activity for the dehydrogenation of 2-propanol—in other words, on the basic property of the catalyst. It is also found, from the mode of change in the yields (17) that acetic acid is more stable than propylene and that acetone is much more reactive than propylene. At any rate, no products of allylic oxidation, such as acrolein and acrylic acid, are obtained by this reaction pathway.

The addition of phosphorus to V_2O_5 induces a large decrease in the oxidation activity, as in the case of the oxidation of *n*-butane (18, 19), while it can change the

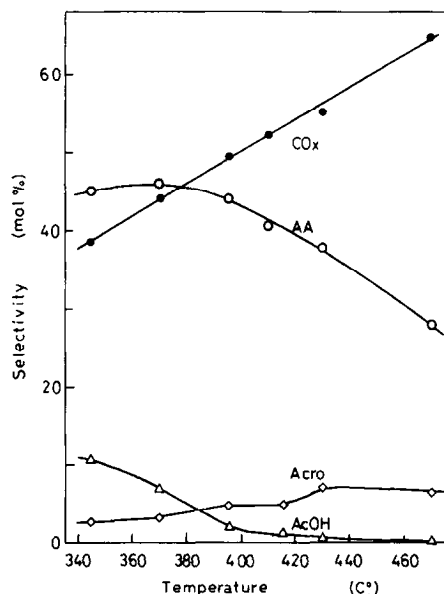


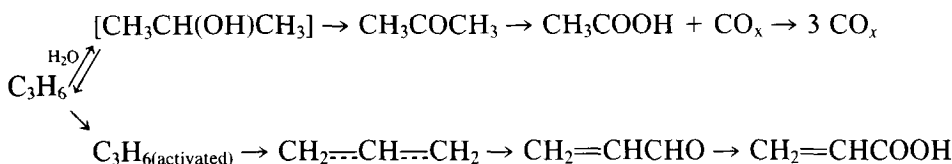
Fig. 16. Effect of the reaction temperature on the product distribution. Symbols are the same as for Fig. 6.

product distribution. As for the effect of phosphorus, many attempts have been made to correlate the catalytic properties of V_2O_5 – P_2O_5 oxides with their structures and/or oxidation states; for example, Schneider (14) proposed that the catalysts containing a crystalline compound—the so-called B-phase having an average valence for vanadium of about 4, which was later assigned to $(VO)_2P_2O_7$ —perform well in the oxidation of *n*-butane. We are sure that the catalytic action is connected with the presence of a certain special phase. However, it has not yet fully explained why the B-phase exhibits a desirable catalytic action; catalysts having a valence for vanadium of about 4 is also obtained by combining another component such as MoO_3 or K_2SO_4 , but these catalysts are not effective for the oxidation of *n*-butane.

In this connection, we would like to explain the catalytic action in terms of the acid-base property of the catalyst, which may be related to the structure and valence state of vanadium. That is, with the increase in the phosphorus content, the

acidic property increases, while the basic property decreases, as has been shown in a previous study (19). The decrease in the basic property induces a decrease in the catalytic activity for the dehydrogenation of 2-propanol, while the increase in the

acidic property induces a strong activation of propylene on the acidic sites, which enables us to direct the propylene to an allylic intermediate. As a result, the hydration pathway and the allylic-oxidation pathway compete with each other:



It seems quite possible that the rate of allylic oxidation is controlled by the rate of allylic-intermediate formation, as in the case of MoO₃-based mixed-oxide catalysts (1). In line with these thoughts, the two rate-controlling steps, the oxidative dehydrogenation of 2-propanol and the formation of the allylic intermediate, can be said to be oxidation reactions; consequently, both of them are affected, to a certain extent, by the oxidizing function of the catalyst, which is related to the basic property of the catalyst (20, 21). However, the oxidizing function is not the sole factor deciding the activity, because the activation of the reactant molecule on the acidic and/or basic sites also plays an important role, especially in the case of mild oxidation (21). In this instance, the increase in the acidic property and the decrease in the basic property serve to promote the allylic oxidation relative to the dehydrogenation of 2-propanol.

As may be seen in Fig. 5, the hydration pathway steadily decreases with the phosphorus content. On the other hand, the allylic oxidation pathway increases with the phosphorus content and attains a maximum at P/V = 1.15 to 1.6 (Fig. 4). With a further increase in the phosphorus content, the surface area markedly decreases (Fig. 3); as a result, a much higher temperature is required to achieve a fixed level of propylene conversion. This may be the reason why

the formation of acrylic acid decreases (Fig. 16).

As is shown in Figs. 2 and 4, the yield of acrylic acid increases linearly with the extent of reaction below 60%, indicating that the consecutive degradation of acrylic acid is small at this extent of reaction. However, with a further increase in the extent of reaction, the slope of the curve, e.g., the selectivity, decreases due to the decomposition of acrylic acid.

As is shown in Figs. 5 and 11, with all the catalysts, the yield of acetic acid passes through a maximum at a propylene conversion of 50 to 80%, indicating that acetic acid is not so stable as acrylic acid on the V₂O₅-P₂O₅-based catalysts.

The effects of the addition of TeO₂ are found to be twofold: (a) an increase in the overall oxidation activity per unit of surface area, and (b) a modification of the product distribution. The latter effect is somewhat complicated. That is, when the TeO₂ content is low (Te/V < 0.04), the formation of acrylic acid and acrolein remains almost unchanged (Figs. 8, 9, and 10), while the formation of acetic acid markedly increases with the TeO₂ content (Fig. 11). However, when the TeO₂ content is high (Te/V > 0.10), the formation of allylic oxidation products, especially acrolein, increases at the expense of a decrease in the formation of acetic acid (Figs. 9, 10, and 11). At least it seems to be clear that the activity for the

oxidation of acrolein relative to that for its formation decreases upon the addition of TeO_2 , though the activity for the formation by itself increases.

In order to clarify the effects of the TeO_2 addition on the acidic property of the catalyst, the catalytic activity for acid-catalyzed reactions, such as the dehydration of 2-propanol and the isomerization of 1-butene, were tested. It was found that the activity decreases only slightly with an increase in the TeO_2 content. On the other hand, the oxidative dehydrogenation of ethanol was chosen as a model base-catalyzed reaction, and the catalytic activity was also studied. However, no clear difference in the activity was observed upon the addition of TeO_2 . Since the $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ by itself is strongly acidic (19), therefore, it seems very hard to detect a subtle change in the acid-base property. Further investigation will be necessary to ascertain the effect of the TeO_2 .

The rate of propylene oxidation is dependent on the oxygen concentration, while it is dependent only faintly on the propylene concentration, in contrast to the case of the $\text{Bi}_2\text{O}_3\text{-MoO}_3$ catalyst (1). Similar results have been observed in the oxidation of *n*-butene (22) and isobutyric acid (23) on the $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ catalyst. Possibly, this may be a common feature observed in every oxidation on an acidic catalyst. As has been mentioned in a previous study (23), the surface of the acidic catalyst is difficultly saturated with oxygen because of its low affinity for oxygen (20, 21), while it is easily saturated with propylene because of its strong affinity for electron-donating (basic) compounds such as propylene.

A comparison of the results shown in Figs. 6 and 13 reveals that the selectivity to allylic oxidation increases with the increase in the oxygen concentration. On the other hand, a comparison of Figs. 6 and 14 reveals that the selectivity decreases with the increase in the propylene concentration. These findings suggest that the presence of vanadium in a high oxidation state favors

the formation of an allylic intermediate rather than the dehydrogenation of 2-propanol. It is plausible that the acid-base property of the catalyst is affected by its oxidation state; an increase in the oxidation state induces an increase in the electronegativity (24), which results in an enhancement of the acidic property rather than the basic property.

As for the formation of acrolein, the results may be summarized as follows: the higher the temperature and the propylene concentration, and the lower the concentrations of oxygen and water vapor, the greater the amount of acrolein obtained. Similar results have been obtained in the oxidation of toluene to benzaldehyde (25). These findings lead us to consider that, in general, aldehydes are relatively stable at higher temperature with a low oxygen/olefin composition and in the absence of water vapor.

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