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Oxidation of Propane to Acrylic Acid on V_2O_5–P_2O_5-Based Catalysts

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V_2O_5–P_2O_5-based oxides were found to be effective as catalysts for the partial oxidation of propane, using gaseous oxygen as an oxidant. Acrylic acid was the sole product other than carbon oxides. The best results for the formation of acrylic acid are obtained with this Te/P/V atomic ratio; 0.10–0.15/1.15/1 oxide catalysts. The yield of acrylic acid attains 10.5 mol%. As the extent of the reaction increases, the selectivity steadily decreases, while the yield first increases and then attains a maximum at a propane conversion of about 50%. The rate of reaction increases with an increase in the concentrations of both oxygen and propane, while it remains almost unchanged with the addition of water vapor to the feed gas. On the other hand, for the formation of acrylic acid, higher concentrations of oxygen and water vapor, a lower concentration of propane, and a lower reaction temperature are found to be favorable. © 1986 Academic Press, Inc.

INTRODUCTION

Most of the work published to date on partial oxidation using gaseous oxygen as an oxidant involves studies of olefins, aromatics, and oxygenates (*1–3*). However, increasing attention has recently been paid to the partial oxidation of paraffinic hydrocarbons, especially *n*-butane (*4–10*). Indeed, it is quite interesting that V_2O_5–P_2O_5-based catalysts exhibit a high selectivity to maleic anhydride from *n*-butane as well as from *n*-butene. As for the partial oxidation of propane, however, little information has been forthcoming, except regarding the photocatalytic oxidation (*11–13*).

In the preceding study (*14*), it has been found that V_2O_5–P_2O_5-based oxides, especially in V_2O_5–P_2O_5–TeO_2, are effective as catalysts for the partial oxidation of propylene to acrylic acid. Thus, it seems that it would be interesting to ascertain the performance of these catalysts for the partial oxidation of propane.

In this study, we first investigated the catalytic behavior of V_2O_5–P_2O_5-based mixed-oxides in the oxidation of propane, and then we have determined the characteristics of the oxidation of propane.

EXPERIMENTAL

Catalysts. The catalysts used in this study were the same as those used in the preceding study (*14*).

Oxidation procedures. The oxidation of propane was carried out with a continuous-flow system. The reactor and the experimental procedures were almost the same as those employed in the preceding study (*14*). Unless otherwise indicated, the reaction conditions were fixed as follows: propane–oxygen–water vapor = 1.85–76.00–22.15 vol%; sum of the flow rates of propane and oxygen, 274 ml (at 20°C)/min (ca. 0.67 mol/h); feed rate of water vapor, 0.195 mol/h; amount of catalyst used, 40 g.

RESULTS

V_2O_5–P_2O_5 Catalysts

The oxidation of propane was performed over a pure V_2O_5 and two V_2O_5–P_2O_5 catalysts with P/V atomic ratios of 0.9 and 1.15. Acrylic acid was the sole product besides carbon oxides. The changes in the yield of acrylic acid and in the selectivity with the extent of the reaction were studied by changing the reaction temperature from 360

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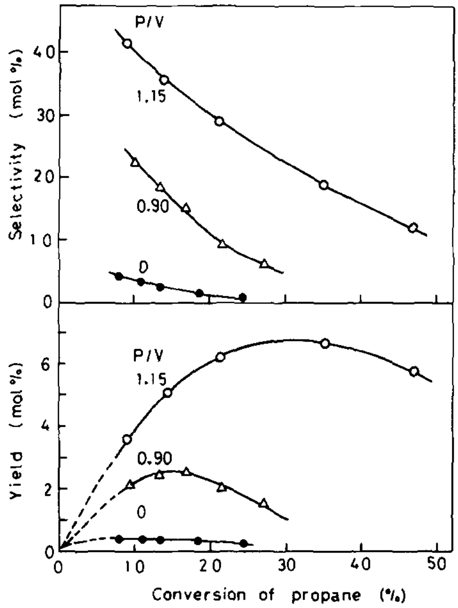


FIG. 1. Effect of the addition of phosphorus on the yield and selectivity in the oxidation of propane to acrylic acid.

to 400°C (Fig. 1). As the extent of reaction increases, the selectivity steadily decreases, while the yield passes through a maximum. For the formation of acrylic acid, the P/V = 1.15 catalyst is clearly more effective than the P/V = 0.9 catalyst.

V_2O_5–P_2O_5–TeO_2 Catalysts

The effect of the addition of TeO_2 to the P/V = 1.15 catalyst was studied in the range of Te/V atomic ratios from zero to 0.20. As is shown in Fig. 2, the formation of acrylic acid increases with the TeO_2 content up to Te/V = 0.10 and passes through a maximum at Te/V = 0.10 to 0.15. The yield attains 9 mol% under the conditions represented in the Experimental section.

V_2O_5–P_2O_5–TeO_2–M_nO_m Catalysts

In order to improve the performance of the Te/P/V = 0.15/1.15/1 catalyst, Nb_2O_5 and ZrO_2 were added in a M/V atomic ratio of 0.10, where M represents the metal atom of the fourth component. It was found that the addition of Nb_2O_5 and ZrO_2 induces a clear increase in the apparent oxidation activity; by way of example, the conversion of propane attains 18, 25, and 42% at 340°C over 30-g portions of the Te/P/V, Nb/Te/P/V, and Zr/Te/P/V oxides, respectively.

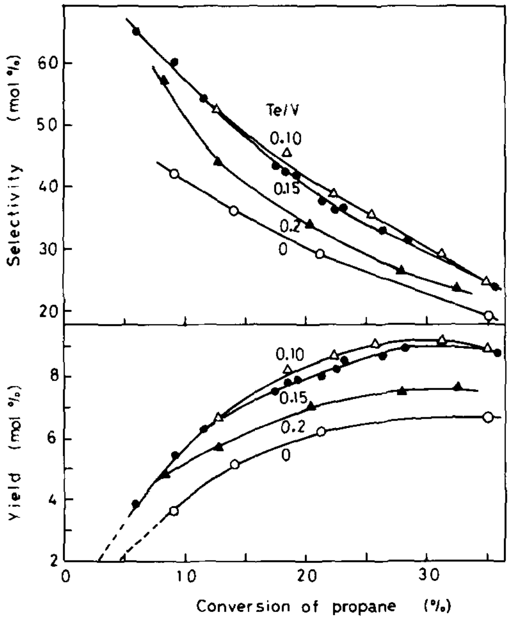


FIG. 2. Effect of the amount of TeO_2 added to P/V = 1.15 oxide on the yield and selectivity in the oxidation of propane to acrylic acid.

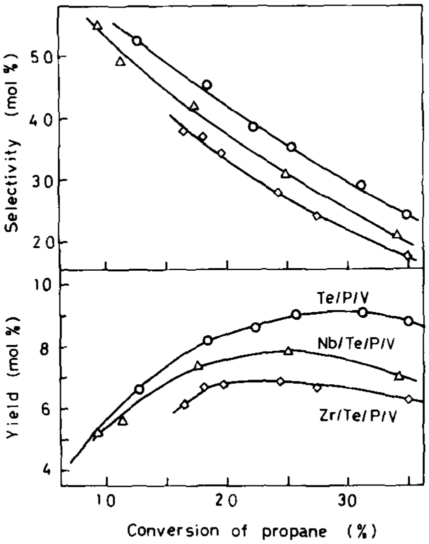


FIG. 3. Effect of the addition of Nb_2O_5 and ZrO_2 to Te/P/V = 0.15/1.15/1 oxide on the yield and selectivity in the oxidation of propane to acrylic acid. Nb/V, Zr/V = 0.10.

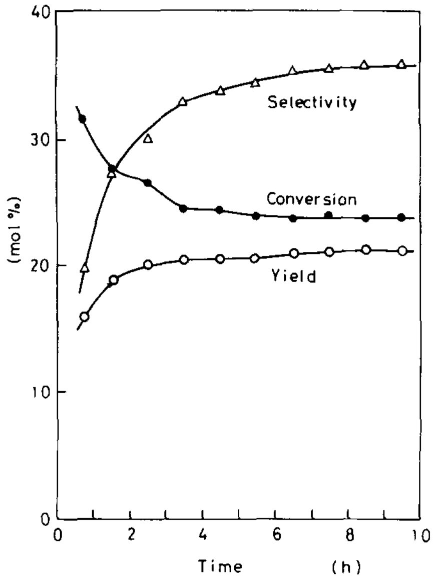


FIG. 4. Stability of the catalytic activity and selectivity. (●) Conversion of propane, (○) yield of acrylic acid ×2, (△) selectivity to acrylic acid.

However, as may be seen in Fig. 3, the addition of Nb_2O_5 and ZrO_2 is unfavorable for the formation of acrylic acid.

Effects of Reaction Variables

The study in the preceding section reveals that the best results for the formation of acrylic acid are obtained with the Te/P/V = 0.10–0.15/1.15/1 catalysts. Thus, the reactions to be discussed below were conducted using the Te/P/V = 0.15/1.15/1 catalyst.

Stability of the catalyst. First, the stability of the catalyst was checked. Figure 4 shows the overall conversion of propane, the yield of acrylic acid, and the selectivity, obtained from the reaction at 400°C using 10 g of the catalyst, as a function of the elapsed time of reaction. It was found that the conversion decreases, while the yield and selectivity increase, with the time on-stream in the first 6 h of operation and that the catalyst reaches a steady state after about 7 h from the start.

Oxygen concentration. The reaction was conducted by changing the initial concentration of oxygen from 6.1 to 81.7 vol%; nitrogen was used as a balance gas. Figure 5 shows the conversion of propane and the yield of acrylic acid obtained from the reaction under the following conditions: temperature, 400°C; propane concentration, 2.0 vol%; water vapor, 16.3 vol%; sum of the flow rates of propane and oxygen, and nitrogen, 400 ml (at 20°C)/min. The propane conversion steadily increases with the increase in the oxygen concentration over the whole range of concentrations.

The yield and the selectivity obtained from the reaction using air as the oxidant are compared in Fig. 6 with those obtained by using oxygen as the oxidant. It is clear that the presence of oxygen in a higher concentration is favorable for the formation of acrylic acid.

Propane concentration. The reaction was conducted by changing the initial concentration of propane from 0.34 to 2.34 vol% in oxygen, while fixing the other conditions. Figure 7 shows the rate of the overall consumption of propane and of acrylic acid formation obtained under the following conditions: temperature, 380°C; sum of the flow rates of propane and oxygen, 400 ml/

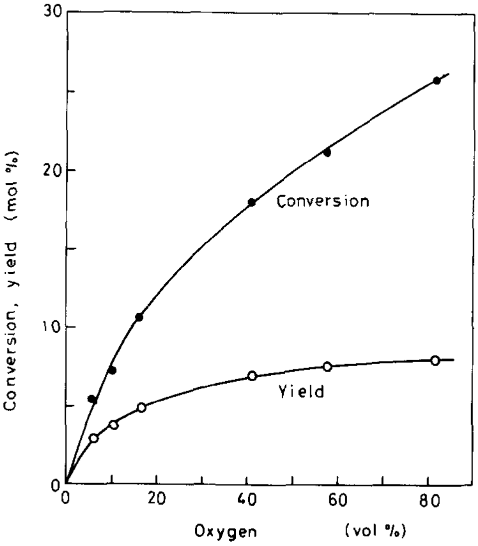


FIG. 5. Effect of the oxygen concentration on the oxidation of propane. (●) Conversion of propane, (○) yield of acrylic acid.

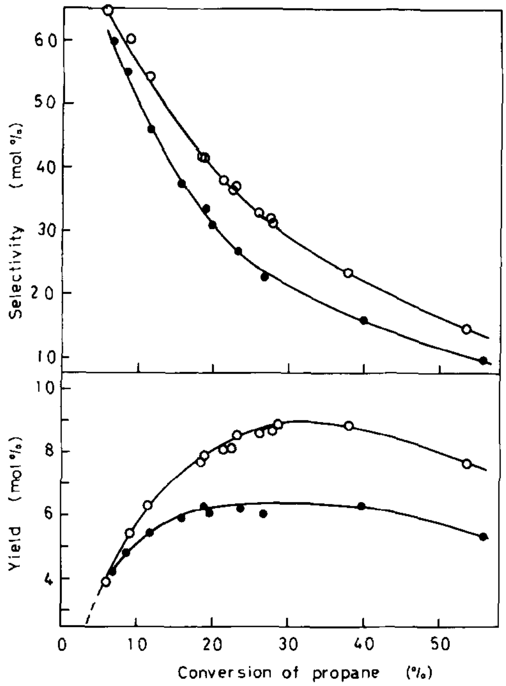


FIG. 6. Comparison of the results obtained by using air as the oxidant with those obtained by using oxygen. Oxidant: (●) air, (○) oxygen.

min; water vapor, 16.3 vol% in oxygen; amount of catalyst used, 40 g. The rates increase almost proportionally to the concentration of propane.

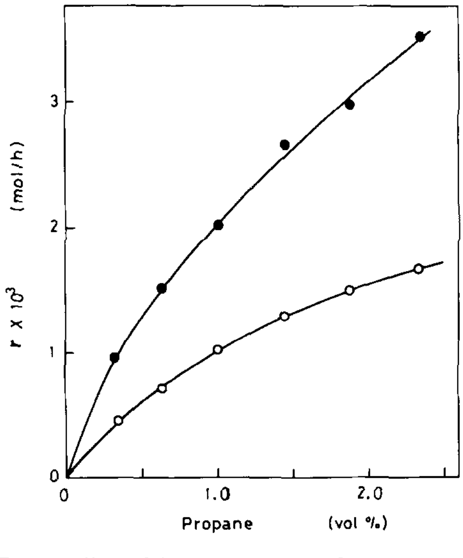


FIG. 7. Effect of the concentration of propane on the rate of oxidation. (●) Rate of propane consumption, (○) rate of acrylic acid formation.

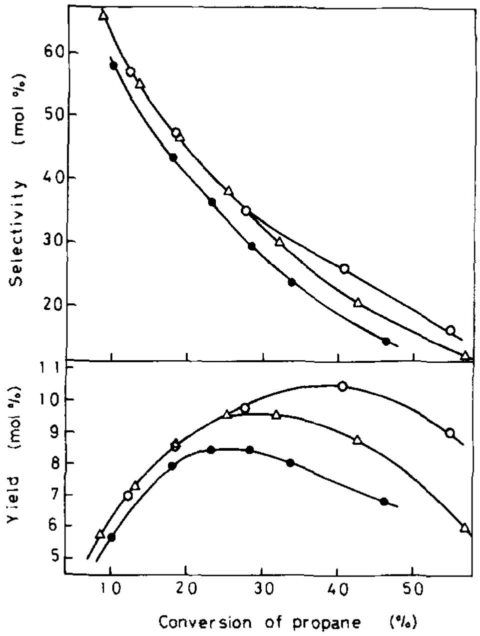


FIG. 8. Effect of the concentration of propane on the yield and selectivity in the oxidation of propane to acrylic acid. Initial concentration of propane: (○) 0.54, (△) 1.0, (●) 2.0 vol% in oxygen.

The effect of the yield and selectivity was then studied (Fig. 8). As the concentration of propane increases, the selectivity decreases more rapidly with the extent of the reaction; on the other hand, the yield attains a maximum at a lower propane conversion. This finding indicates that the consecutive oxidation of acrylic acid is enhanced with the increase in the propane concentration.

Water vapor. The reaction was conducted by changing the content of water vapor in the feed gas from zero to 36.2 vol%, while fixing the other conditions; flow rate of propane, 6.5 ml/min; flow rate of oxygen, 264 ml/min. The conversion of propane at 390°C, corrected for the variation in the total flow rate due to the change in the feed rate of water vapor, remained almost unchanged at about 30% with the change in the content of water vapor.

Figure 9 shows the effect on the yield and selectivity. It is evident that the formation of acrylic acid increases steadily with the increase in the content of water vapor.

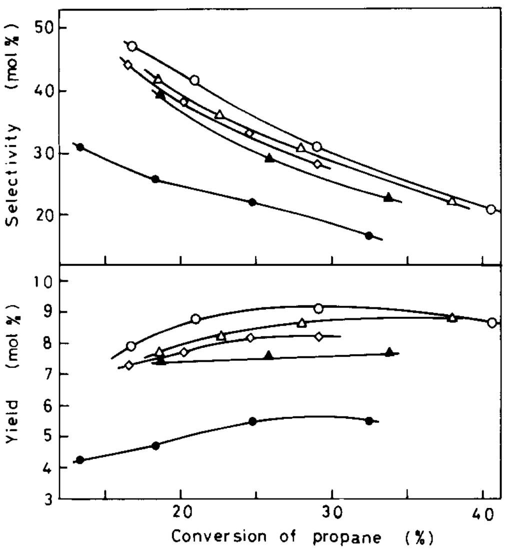


FIG. 9. Effect of the concentration of water vapor on the yield and selectivity in the oxidation of propane to acrylic acid. Water vapor concentration: (●) 0, (▲) 7.7, (◇) 12.4, (△) 22.1, (○) 36.2 vol%.

Reaction temperature. The effect of the reaction temperature on the selectivity was studied by comparing the yields at two fixed levels (12 and 23%) of propane conversion; the results had been obtained by changing the amount of catalyst used from 2.5 to 40 g (Fig. 10). As the reaction temperature is elevated, the selectivity to acrylic acid decreases.

DISCUSSION

Oxidation Activity

As is shown in Fig. 5, the rate is dependent on the oxygen concentration over the whole range of concentrations, as in the case of the oxidation of propylene (*14*). As has been mentioned in the preceding study (*14*), this oxygen dependency seems to be a common feature observed in oxidations on an acidic catalyst.

On the other hand, as may be seen in Fig. 7, the rate is dependent on the propane concentration over a wide range of concentrations. This finding is different from those in the oxidations of propylene (*14*), isobutyric acid (*15*), and butenes (*16*), while it is similar to that obtained in the oxidation of *n*-butane on composite catalysts consisting of salts of molybdophosphoric acid and a vanadium promoter (*17*). Possibly, this dependency is also a common feature observed in the oxidation of paraffinic hydrocarbons. It is plausible that the catalyst is hard to saturate with the reactant, for paraffinic hydrocarbons are deficient in their affinity for a catalyst.

Selectivity

In order to ascertain whether propylene is an intermediate in the oxidation of propane to acrylic acid, another series of experiments were performed using a high propane concentration (48 vol% in air), as Centi *et al.* (*5*) did for the oxidation of *n*-butane. In these conditions, oxygen is the limiting reagent and the conversion of propane is less than about 5%. The formation of propylene as well as acrylic acid and carbon oxides was observed even in the presence of oxygen. Figure 11 shows the conversion of oxygen and the rates of formation of the three products as a function of the reaction temperature. The formation of propylene increases gradually as the extent of oxygen consumption increases and it attains about 2 mol% of the charged propane at 470°C. These results are in conformity with those for the oxidation of *n*-butane (*5*) and support that propylene

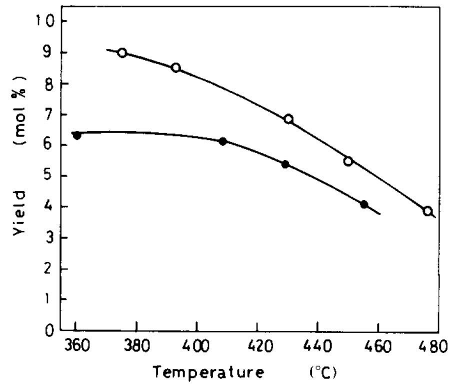
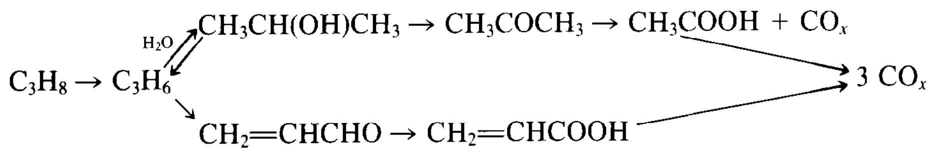


FIG. 10. Effect of the reaction temperature on the yield of acrylic acid at fixed levels of propane conversion. (●) conversion = 12%, (○) conversion = 23%.

is formed by the oxidative dehydrogenation of propane.

By analogy with the oxidation of *n*-butane (*17*), the oxidation of propane must proceed through the following reaction pathway:



$$\begin{tikzcd}[column sep=small] & CH_3CH(OH)CH_3 \arrow[r] & CH_3COCH_3 \arrow[r] & CH_3COOH + CO_x \arrow[dr] & \\ C_3H_8 \arrow[r] & C_3H_6 \arrow[u, "H_2O"] \arrow[d] & & & 3\ CO_x \\ & CH_2{=}CHCHO \arrow[r] & CH_2{=}CHCOOH \arrow[urr] & & \end{tikzcd}$$

The yield of acrylic acid may be dependent on two factors: (i) the rate of the allylic oxidation of propylene relative to that of the oxyhydration of propylene to acetone, and (ii) the rate of the formation of acrylic acid relative to that of the consecutive oxidation of acrylic acid. The first factor has been discussed in the preceding study (*14*).

For a understanding of the second factor, the catalytic activity was studied for the oxidation of various compounds related to the oxidation of propane. The initial concentrations of each reactant were: propane and propylene = 2.0, acetic acid = 2.5, acrylic acid = 2.2, acrolein = 2.5 vol% in oxygen. The content of water vapor was 16.3 vol%, the feed rate of oxygen was 390 ml/min, and the amount of catalyst used was 10 g. The conversions of each reactant are plotted as a function of the reaction temperature in Fig. 12.

It was found that the reactivity of each reactant is ordered in this sequences:

acrolein > propylene > acetic acid
> acrylic acid > propane.

From these results, the product distributions obtained in the oxidations of propane and propylene (*14*) can be understood. That is, in the oxidation of propane, the formation of acrylic acid is limited by its consecutive oxidation, because acrylic acid is more reactive than propane, and the formation of propylene, acrolein, and acetic acid is not observed in the presence of an excess of oxygen because these intermediate compounds are much more reactive than propane.

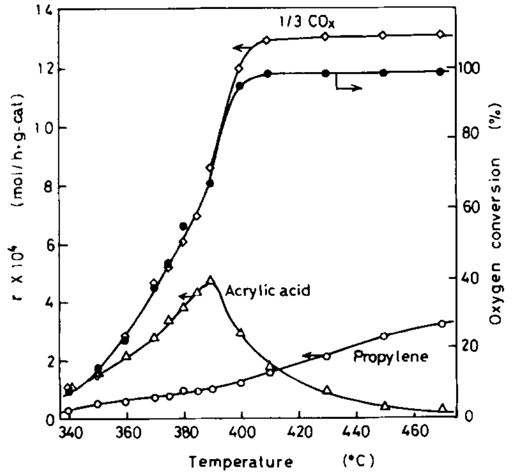


FIG. 11. Effect of the temperature on the rates of formation in the oxidation at a high propane concentration. Conditions: flow rate of propane, 100 ml/min; flow rate of air, 110 m/min; catalyst, Te/P/V = 0.15/1.15/1 oxide (10 g).

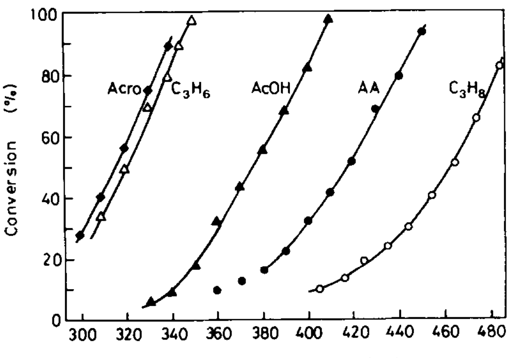


FIG. 12. Dependence of the overall conversion on the reaction temperature. (◆) Acrolein, (△) propylene, (▲) acetic acid, (●) acrylic acid, (○) propane.

On the other hand, in the oxidation of propylene (*14*), the consecutive oxidation of acrylic acid is small, because acrylic acid is much more stable than propylene, and the formation of acrolein and acetic acid is observed because the reactivities of these compounds are close to that of propylene.

The Yield of acrylic acid from propane is much lower than that of maleic anhydride from *n*-butane (*4, 5, 8, 10*). This difference in the yield may be attributed to the difference in the above-mentioned two factors; that is, (i) the depression of the oxyhydration of propylene is more difficult than that of butenes (*14*), and (ii) acrylic acid is much less stable than maleic anhydride.

As is shown in Fig. 10, with the elevation of the reaction temperature, the selectivity to acrylic acid falls, especially above 400°C, indicating that the degradation of acrylic acid is enhanced more strongly than its formation. Therefore, it is to be noted that the possession of a sufficiently high oxidation activity is essential for a catalyst to achieve a good selectivity to acrylic acid.

In line with this fact, the effect of the concentrations of oxygen and propane on the yield of acrylic acid can be understood. That is, as the oxygen concentration increases and the propane concentration decreases, the temperature required to achieve a fixed level of conversion falls, resulting in an increase in the yield.

The effect of water vapor on the yield can also be understood from the finding (*14*) that the formation of acrylic acid from propylene is enhanced as the content of water vapor increases.

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