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Oxidation of propane over V_2O_5–P_2O_5-based catalysts at relatively low temperatures

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Abstract

Oxidation of propane was performed over a V_2O_5–P_2O_5 (P/V atomic ratio=1.2) catalyst in the presence of a large excess of oxygen at relatively low temperatures of 270–360°C. A long contact time of 23–70 s was required. The main products were acrylic acid, acetic acid, and CO. The presence of water vapor was indispensable to obtain acrylic acid, while it was not required for the formation of acetic acid. The one-pass yields of both acrylic acid and acetic acid reached 7.5 mol% at the propane conversion of 45%. The selectivities in the oxidation of propane to acrylic acid and to acetic acid are almost the same as those obtained in the oxidation of propene, respectively, when the conversions are low. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Propane oxidation; Acrylic acid; Acetic acid; Water-vapor effect; Vanadyl pyrophosphate

1. Introduction

It is predictable on the analogy of oxidation of *n*-butane to maleic anhydride that propane is oxidized to acrylic acid over catalysts having both redox and strongly acidic functions [1]. We reported previously [2,3] the performances of catalysts based on vanadyl pyrophosphate [$(VO)_2P_2O_7$] in the oxidation of propane. Recently, the same reaction has also been studied using catalysts based on heteropoly acid [$H_3PMo_{12}O_{40}$] [4–6]. The catalytic performances of heteropoly compounds seem to be lower than those of V–P-based mixed oxides consisting of vanadyl pyrophosphate, furthermore the latter catalysts are much more stable than the heteropoly compounds. The yields of acrylic acid are markedly lower than those of maleic anhydride obtained in the oxidation of *n*-butane. The following conclusions were drawn [2,3,6]:

1. propane is much less reactive than *n*-butane,
2. suppression of dehydration of 2-propanol is more difficult than that of 2-butanol, and
3. acrylic acid is much more reactive than maleic anhydride.

It was found in the previous study [2] that the selectivity in the oxidation of propane to acrylic acid increases as the reaction temperature is dropped. The aim of this study was to gain more insight into the oxidation of propane performed especially at low temperatures.

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2. Experimental

The catalyst used in this study was a V_2O_5–P_2O_5, with a P/V atomic ratio of 1.2, consisting of $(VO)_2P_2O_7$, which was prepared according to patented procedures [7]. The surface area measured by the BET method was 17.3 m^2/g.

The reaction was carried out with a continuous-flow system at atmospheric pressure. The reactor was made of a Pyrex glass tube, 80 cm long and 2.3 cm i.d., mounted vertically and heated with an electric furnace. A mixture of either propane–oxygen or propene–oxygen was fed in from the top of the reactor with water being introduced by a syringe pump. The feed rate of propane or propene was fixed at 6.75 mmol/h (2.70 ml/min), and that of oxygen was 250 mmol/h (100 ml/min), while the feed rate of water vapor was varied from 0 to 530 mmol/h. The amount of catalyst used was fixed at 120 ml (77 g). The contact time (c.t.) defined as (volume of catalyst)/(flow rate of gaseous feed) was varied in the range of 23–70 s depending on the variation in the feed rate of water vapor. The reaction temperature was in the range of 270–360°. The other reaction procedures and the method of analysis were the same as those described in the previous works [2,3].

3. Results

3.1. Oxidation of propane

Fig. 1 shows the conversion of propane as a function of the reaction temperature. As the feed rate of water vapor increases, the contact time becomes short, as a result, higher temperatures are required to achieve a sufficient level of propane conversion. It was found that the oxidation of propane takes place enough at low temperatures of 300–350°C under the reaction conditions used. It should be noted that the reaction rate is markedly suppressed by the presence of water vapor.

The products were acrylic acid, acetic acid, and CO with small amounts of CO_2. No other products such as propene, acetone, acrolein were detected. Fig. 2 shows the yields of acrylic acid obtained at different feed rates of water vapor as a function of the conversion of propane: the slopes from the origin indicate the selectivities to acrylic acid.

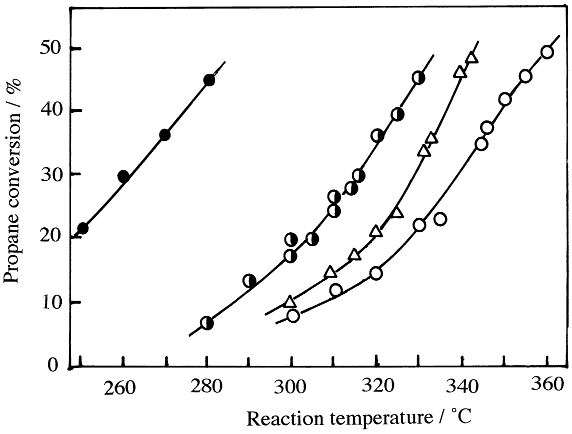


Fig. 1. Conversion of propane as a function of the reaction temperature. Symbols: [feed rate of water vapor; mmol/h], {contact time; s}. (●) [0] {70}; (◐) [109] {50}; (△) [265] {35}; and (○) [530] {23}.

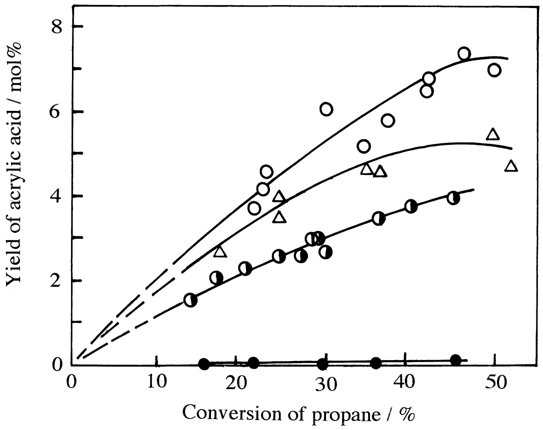


Fig. 2. Yield of acrylic acid as a function of propane conversion. Symbols are the same as those in Fig. 1.

As the conversion of propane increases, the yield increases and passes through a broad maximum at the conversion of around 50%. It is interesting to note that acrylic acid is not obtained in the absence of water vapor and the formation of acrylic acid increases largely as the feed rate of water vapor increases. This finding indicates that the presence of water vapor is indispensable for the formation of acrylic acid from propane. The yield of acrylic acid reached 7.5 mol% at the propane conversion of 46%; the selectivity is about 15 mol%.

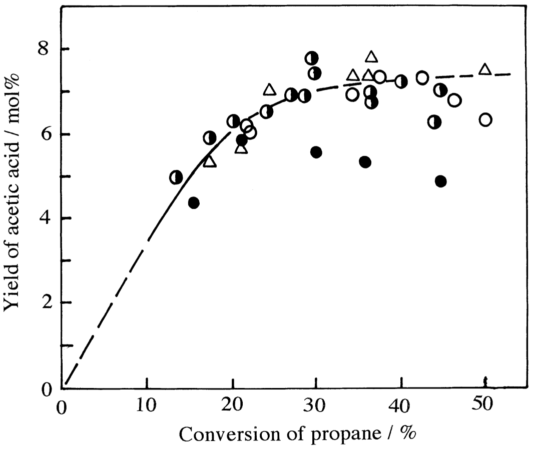


Fig. 3. Yield of acetic acid as a function of propane conversion. Symbols are the same as those in Fig. 1.

The yields of acetic acid are plotted in Fig. 3. The yield increases as the propane conversion increases upto about 25%, and then it levels off; the yield cannot exceed 7.5 mol% due to the consecutive decomposition of acetic acid. The effect of water vapor on the selectivity from propane to acetic acid is not clear. The selectivity at a low conversion of around 20% was about 30 mol%. These findings indicate that acrylic acid is more stable than acetic acid over the catalyst used in agreement with the results obtained in higher temperatures [2].

3.2. *Oxidation of propene*

Oxidation of propene was also performed at a temperature from 260°C to 330°C in a manner similar to that of propane. The main products were acrylic acid, acetic acid, and CO with small amounts of CO_2, as in the case of the oxidation of propane. However, small amounts of acetaldehyde, acrolein, and acetone were detected; the yield of acetaldehyde was about 0.4 mol% in the presence of water vapor and 0.7 mol% in the absence of water vapor at the propene conversion ranging from 20% to 70%; the yield of acrolein was about 0.6 mol% in the presence of water vapor and 0.2 mol% in the absence of water vapor at the conversion from 20% to 70%; and the yield of acetone was less than 0.1 mol%.

Fig. 4 shows the yield of acrylic acid as a function of the conversion of propene. The formation of acrylic acid increases as the feed rate of water vapor increases much like that from propane. However, the selectivity to acrylic acid does not decline with an increase in the conversion unlike the case of the propane oxidation. This finding suggests that the consecutive decomposition of produced acrylic acid is very small under the

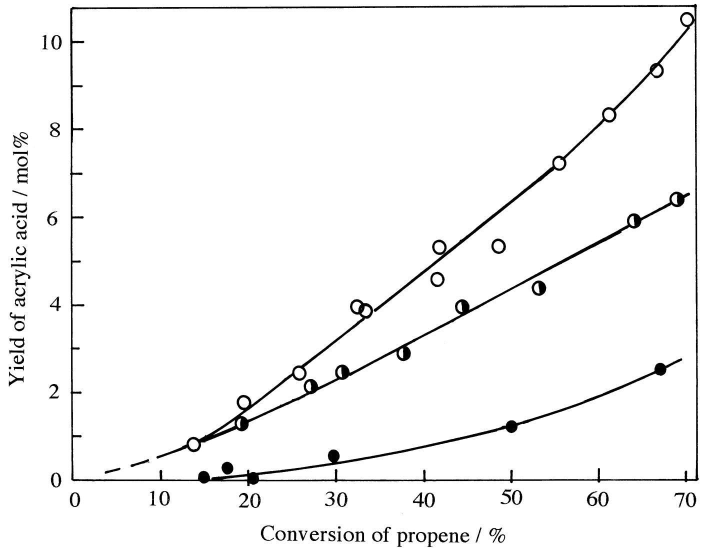


Fig. 4. Yield of acrylic acid as a function of propene conversion. Symbols are the same as those in Fig. 1.

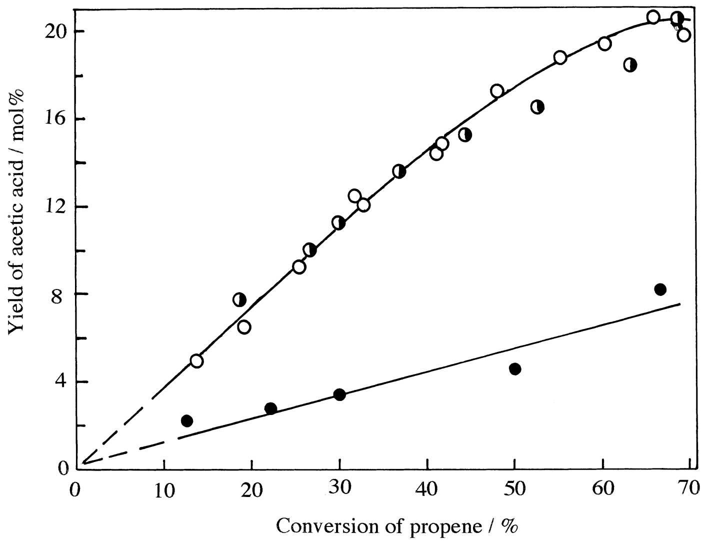


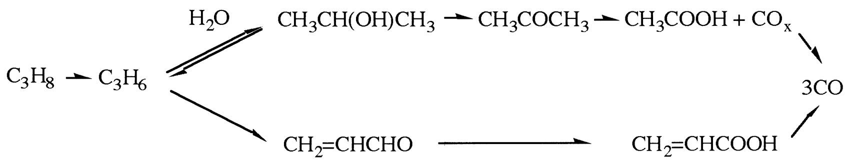
Fig. 5. Yield of acetic acid as a function of propene conversion. Symbols are the same as those in Fig. 1.

conditions used in the oxidation of propene, unlike in the case of propane. When the feed rate of water vapor was high, 530 mmol/h, the selectivity was about 15 mol%; this value is the same as that obtained in the oxidation of propane.

The yields of acetic acid are plotted in Fig. 5. The yield increases almost linearly with an increase in the propene conversion up to 65%. The selectivity was about 35 mol%. This value is almost the same as that obtained at a low conversion in the oxidation of propane. As in the case of the oxidation of propane, the yield of acetic acid is not affected with a large variation in the feed rate of water vapor from 109 to 530 mmol/h, though the yield was clearly lower in the absence of water vapor.

4. Discussion

By analogy with the oxidation of *n*-butane to maleic anhydride [8], the following reaction pathway was proposed for the oxidation of propane [2,6].



The reaction may be started from the oxidative dehydrogenation of propane to form propene. Probably, this step should be the slowest step and it is markedly suppressed by the presence of water vapor. Then, a part of the produced propene is hydrated to form 2-propanol; this step is considered to be rapid enough and it is in equilibrium during the reaction. By the oxidative dehydrogenation of 2-propanol, acetone is formed. The produced acetone is quickly decomposed to form acetic acid and CO. The obtained experimental results (Figs. 3 and 5) indicate that the presence of a large amount of water vapor does not affect the selectivity of the steps from propene to acetic acid.

On the other hand, another part of the propene is transformed to acrolein by an allylic oxidation and the produced acrolein is quickly oxidized to form acrylic acid. The results shown in Figs. 2 and 4 indicate that the presence of water vapor is required for the formation of acrylic acid. It is hard to consider that water takes part directly in the allylic oxidation. Indeed, it has been found [2] that at a higher temperature of

390°C, a small amount of acrylic acid is obtained from propane even in the absence of water vapor.

These findings lead us to the following conclusion that the water vapor plays a role in removing quickly the produced acrylic acid from the surface and that this role is important especially in the case of reaction at a low temperature. Further, it is considered that acrylic acid is adsorbed more strongly than acetic acid on the surface.

Interestingly, the selectivity to acrylic acid in the oxidation of propane is almost the same as that in the oxidation of propene, and furthermore, the selectivity in the oxidation of propane to acetic acid at a low conversion of about 20% is also near to that in the oxidation of propene. These findings suggest that the oxidative dehydrogenation of propane to propene takes place with a very high selectivity when the reaction is performed at low temperature. As a result, it is considered that the most important function required to the catalysts for production of acrylic acid from propane is the suppression of oxidative dehydrogenation of 2-propanol to acetone.

It is known that dehydrogenation of alcohol to ketone or aldehyde is promoted by the action of basic sites of catalyst. On the other hand, the redox function is related to the basic property of catalyst [1]. The basic sites play two contradictory functions for the reaction. Therefore, it is believed that the control of basic property is the key to obtaining a good catalyst.

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