V–Zr–P oxide catalysts for highly selective oxidation of propane to acrylic acid

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V–Zr–P oxide catalysts have been prepared and exhibited high selectivity in the oxidation of propane to acrylic acid.

The selective oxidation of lower alkanes to other chemicals is attracting attention for economic reasons and their availability. The best-known oxidation of lower alkanes is the selective oxidation of *n*-butane to maleic anhydride over vanadium phosphorus oxide catalysts (VPO).[1] Moreover, oxidation of propane to propylene,[2–4] acrolein[5] and acrylonitrile[6] has been widely developed. It was found first by Ai[7,8] that a VPO based catalytic system could directly oxidize propane to acrylic acid effectively. The V_2O_5–P_2O_5–X_nO_m (X_nO_m = SO_3, TeO_2, Nb_2O_3, Sb_2O_3, SiO_2 and B_2O_3) type catalysts have been tested and the catalytic performance in this process is clearly improved. However, the reaction carried out on VPO catalysts at relatively high temperature (400 °C) not only results in a low selectivity to acrylic acid, but also leads to serious formation of coke on the catalyst surface and shortage of lifetime. To solve these problems, we have reported the use of a titania–silica xerogel supported VPO catalyst in this reaction[9] which showed highly selective oxidation of propane to acrylic and acetic acid at low temperature (300 °C). So far, the yield and selectivity to acrylic acid for all developed catalysts are too low to be applied at commercial level. For this reason, we sought to develop a new catalyst that possesses good performance at low temperature in order to give high yield and selectivity to acrylic acid without coking.

In our study, it was demonstrated that V–Zr–P (Zr : V = 0.5) oxide catalyst showed significant high selectivity and yield to acrylic acid at 340 °C, and had the potential for practical use.

V–Zr–P oxide catalysts were prepared by the following procedure: a mixture of V_2O_5 and $ZrOCl_2 \cdot H_2O$ in stoichiometrical atomic ratio (Zr : V) was reduced by refluxing in a solution of isobutanol (20 ml)–benzyl alcohol (10 ml) for 12 h; a black blue or gray suspended precipitate formed. Then, an appropriate amount of 85% H_3PO_4 [atomic ratio P : (Zr + V) = 1.0] was added to the solution, which was refluxed for 6 h to give a light blue–green suspended precipitate and a black–blue solution. The precipitate was filtered off and the obtained paste was dried in an oven at 120 °C overnight. The resulting precursor was ground and sieved to obtain a 40–60 mesh size portion. VPO (V : P = 1.0) and ZrPO (Zr : P = 1.0) catalysts were also prepared by the same procedure to enable comparison. The activation of precursor and oxidation of propane were carried out in a continuous tubular flow fixed-bed microreactor. The precursor of the V–Zr–P oxide catalyst (1.0 ml) was packed into a stainless steel reactor (id: 6.0 mm, length: 20 cm) and the temperature was raised to 773 K at a rate of 20 K min^{-1} in a mixture of air–propane–water vapor (75.6 : 1.2 : 23.2) at a rate of 20 ml min^{-1} for 12 h. The sample was then cooled to the reaction temperature within 6 h.

The X-ray diffraction patterns for all the catalysts are in Fig. 1. Lines at 2θ = 23.1, 28.4 and 29.9° are attributed to $(VO)_2P_2O_7$, and those at 2θ = 22.0, 26.0 and 28.9° are attributed to $VOPO_4$, respectively.[10] It can be seen that the bare VPO catalyst is mainly constituted of $(VO)_2P_2O_7$ with some $VOPO_4$. The X-ray line due to $(VO)_2P_2O_7$ broadened and diminished with increase of the atomic ratio of Zr : V in the V–Zr–P oxides. Only small broad diffraction peaks were detected when Zr : V was raised to 1.0, indicating that $(VO)_2P_2O_7$ starts to become disordered. No distinct XRD line can be found for ZrPO, suggesting that ZrPO is an amorphous material. In addition, no zirconium phosphate was evidenced for any V–Zr–P oxides, implying that ZrPO can only disperse into the structure of VPO or form a solid solution with $(VO)_2P_2O_7$. It is also interesting to observe that the $VOPO_4$ phase disappears as Zr : V is increased to 0.25, which suggests that its formation has been suppressed.

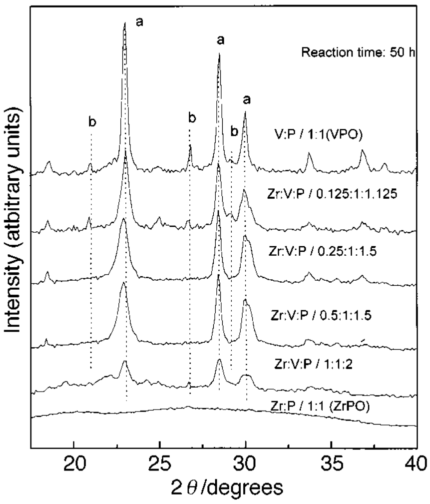

Fig. 1 XRD patterns of V–Zr–P oxide catalysts; (a) $(VO)_2P_2O_7$, (b) $VOPO_4$.

All catalysts employed in this study were tested for the selective oxidation of propane to acrylic acid. The optimal results summarized in Table 1 show that ZrPO is inert to this reaction. For VPO catalyst, the yield and selectivity to acrylic acid are 11.2 and 48.1%, respectively. With the addition of Zr, the yield and selectivity increase sisgnificantly in comparison with the VPO catalyst. As Zr : V is changed from 0.125 to 0.5, the selectivity increases from 70.0 to 81.0% and the yield increases from 13.5 to 14.8%. With continuous increasing ratio of Zr : V to 1.0, the activity and selectivity start to decrease.

It can be seen in Fig. 2, that the temperature for achieving maximum selectivity shifts from 400 (VPO) to 340 °C (V–Zr–P

Table 1 The performance of V–Zr–P oxide catalysts[a]

V : Zr atomic ratio	T/°C	Conv. (mol%)	Yield (mol%)	Sel. (mol%)
1 : 1	340	16.1	12.7	70.3
1 : 0.5	340	17.5	14.8	81.0
1 : 0.25	360	18.4	14.2	71.0
1 : 0.125	380	18.5	13.5	70.0
VPO	400	23.0	11.2	48.1
ZrPO	400	—	—	—

[a] *Reaction conditions*: GHSV = 1000 h^{-1}, feed gas = air–propane–water = 73.4 : 3.2 : 23.4, time = 50 h, cat. 1.0 g; analysis: on-line gas chromatograph.

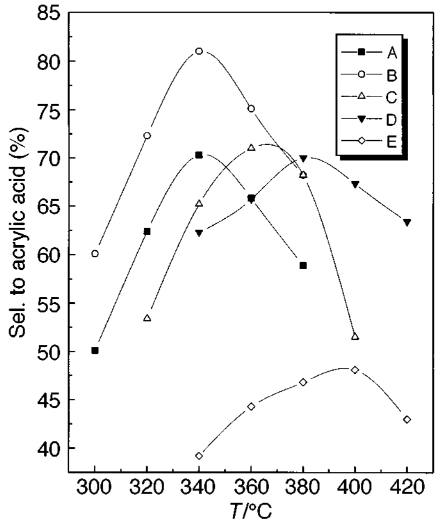

Fig. 2 Dependence of selectivity of acrylic acid on reaction temperature; (A) Zr : V : P = 1 : 1 : 2, (B) Zr : V : P = 0.5 : 1 : 2, (C) Zr : V : P = 0.25 : 1 : 2, (D) Zr : V : P = 0.125 : 1 : 2, (E) VPO. Reaction conditions: GHSV = 1000 h^{-1}, feed gas = air–propane–water vapor (73.6 : 3.2 : 23.2), time = 50 h.

oxide, Zr : V = 0.5). It is well known that lowering temperature is favorable for reducing coke formation and beneficial in increasing the lifetime of the catalyst. Fig. 3 shows that V–Zr–P (Zr : V = 0.5) oxide catalyst shows significantly higher catalytic stability than that of VPO after 100 h of operation.

Comparison of XRD patterns with the catalytic properties of V–Zr–P oxides, as shown in Fig. 1 and Table 1, suggests a correlation of XRD line strength for $(VO)_2P_2O_7$/$VPOP_4$ with the catalytic performance of the catalyst. $(VO)_2P_2O_7$ most likely acts as the active phase in oxidation of propane as found in the VPO based catalytic system in oxidation of butane.[10] Further, the addition of amorphous materials in the structure of V–Zr–P oxide may effectively disperse VO_x or $(VO)_2P_2O_7$, and make an important contribution in enhancing the selectivity of catalyst.

In summary, V–Zr–P oxide catalysts exhibit satisfactory performance for selective oxidation of propane to acrylic acid. The best result, 14.8% yield and 81.0% selectivity, is shown by the catalyst with V : Zr : P = 1 : 0.5 : 1.5, at an optimum reaction temperature of 340 °C. It is clear that V–Zr–P oxide catalysts are promising for use in the selective oxidation of propane to acrylic acid.

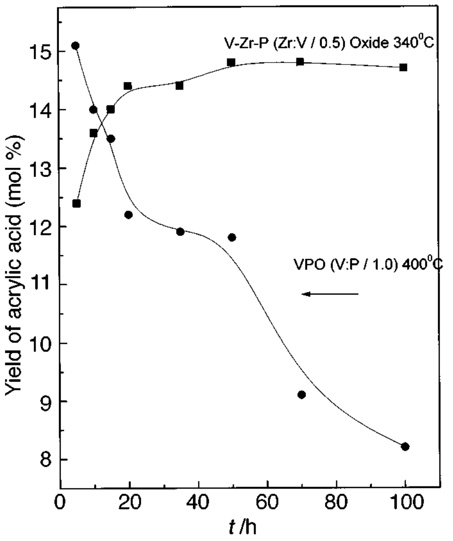

Fig. 3 Dependence of reaction time on the yield of acrylic acid. Reaction conditions: GHSV = 1000 h^{-1}, feed gas = air–propane–water vapor (73.6 : 3.2 : 23.2).

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