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Dispersed vanadium phosphorus oxide on titania–silica xerogels: highly active for selective oxidation of propane

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Dispersed vanadium phosphorus oxide on titania–silica xerogels have been prepared and used as catalysts for the selective oxidation of propane.

Vanadium oxide based catalysts have been used worldwide for their effect on the oxidation reaction of alkanes:[1] especially, vanadium phosphorus oxide (VPO) catalysts have been successfully applied for the selective oxidation of *n*-butane to maleic anhydride.[2] Besides this, it has also been found that vanadium phosphorus oxide based catalysts are effective for the selective oxidation of propane to organic compounds,[3,5] such as acrylic acid, acetic acid, acrolein and acetone. However, the reaction carried out on VPO catalysts at relatively high temperature (~380°C) not only results in a low selectivity to organic compounds, but also leads to a serious formation of coke on the catalyst surface. For this reason, the application of VPO catalysts to the partial oxidation of propane is limited. We sought to develop a new catalyst for the propane oxidation reaction, which can possess good activity at low temperature in order to prevent coking and give high selectivity to organic compounds.

Amorphous TiO_2–SiO_2 xerogel is a good matrix material because it possesses all of the necessary properties such as (1) high thermal stability, (2) inertness in the oxidation of propane, (3) high surface area, (4) oxygen storage and transfer functions. In this context, we developed highly dispersed titania–silica (TiO_2–SiO_2) xerogel-supported VPO catalysts. It was demonstrated that highly dispersed VPO in the titania–silica xerogels exhibited good selective oxidation of propane at low temperature in comparison with bare VPO catalyst, and has a potential for being put to practical use.

The aimed-for catalysts were prepared by the following procedure. First, the VPO catalyst was prepared according to patented procedures:[5] V_2O_5 (5 g) was reduced by refluxing in a solution of benzyl alcohol (10 ml)–2-methyl-1-propanol (20 ml) for 6 h; a black-blue suspended precipitate formed. Then, 4 ml of 85% H_3PO_4 and 20 ml of 2-methyl-1-propanol were added to the solution and it was refluxed again for 2 h; a light blue-green suspended precipitate formed. The solution was filtrated and the final paste was dried in an oven at 120 °C overnight. The V : P atom ratio is 1.1 : 1. Second, the amorphous TiO_2–SiO_2 xerogel is prepared as follows.[6] Silicon tetraethyl oxide (50 ml) was dissolved in absolute ethanol (100 ml) and 15 ml HCl solution (0.15 mol l^{-1}). The solution was heated to 60 °C for 1.5 h and then cooled to room temperature, followed by addition of 3 mmol of $Ti(OPr^i)_4$. The formed gel was then left in an open beaker to allow slow evaporation of the solvent; a brittle 5% TiO_2–SiO_2 xerogel formed after 24 h. The xerogel was ground and dried in air overnight at 100 °C. Finally, the required amounts of $VOHPO_4 \cdot \frac{1}{2}H_2O$ and TiO_2–SiO_2 were mechanically mixed by grinding and sieved to give 60 to 80 mesh size portions.

The catalysts were activated in a stream of a gaseous mixture of oxygen, propane and water vapor at 500 °C. As shown in Fig. 1(*a*) the XRD (X-ray diffraction) spectrum shows that the VPO catalyst used in our study has the typical diffraction peaks at $2\theta = 17.1°$, 19.2°, 28.5° and the TiO_2–SiO_2 xerogel is amorphous without any peak detected [Fig. 1(*g*)]. VPO (10.2 wt%)/TiO_2–SiO_2 calcined at 300 °C [Fig. 1(*f*)] shows small peaks at 17.1°, 19.2°, 28.5°, which are the typical peaks for VPO. The same sample calcined at 500 °C shows no peaks for VPO. This demonstrates that VPO has been highly dispersed on the surface of the titania–silica xerogel. The small peaks at 17.1°, 19.2°, 28.5° appear again as the VPO loaded amount is increased from 10.2 to 16.7 to 23.1 wt%; this is because a multilayer of VPO is formed as the loaded amount increases.

All catalysts employed in this study were tested for the selective oxidation of propane; the results are presented in Table 1. It is shown that the TiO_2–SiO_2 xerogel has no effect on the model reaction. At 300 °C, the supported catalysts showed better performances than VPO alone. VPO(10.7 wt% or 16.7 wt%)/TiO_2–SiO_2 catalysts gave a selectivity to acids up to 55.3% and 61.2% at propane conversion of 18.3% and 21.8%, respectively. As a comparison, under the same reaction conditions, the conversion of propane and selectivity to acids are 15.0% and 47.2% over the unsupported VPO catalyst. It is clear that the selectivity to acid has been improved after dispersing VPO on the TiO_2–SiO_2 matrix.

The dependence of organic acid selectivity on temperature over supported VPO/TiO_2–SiO_2 has been investigated. Dispersed VPO on TiO_2–SiO_2 enhanced the selectivity greatly at low temperature. In the case of VPO(16.7 wt%)/TiO_2–SiO_2 (see Fig. 2), the maximum in the selectivity-to-acid curve increased to 61.2% at 300 °C, while the selectivity reached

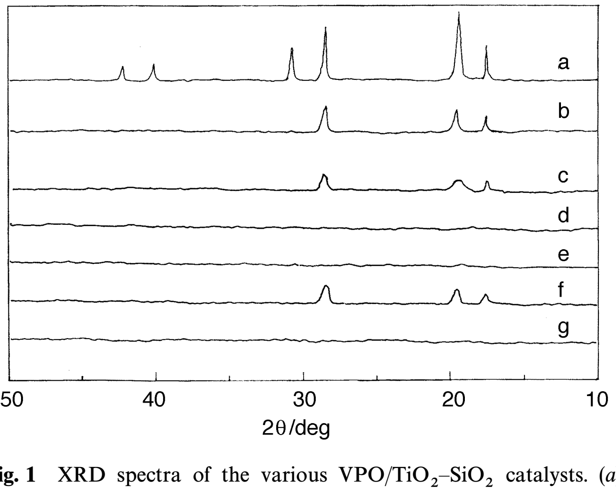

Fig. 1 XRD spectra of the various VPO/TiO_2–SiO_2 catalysts. (*a*) VPO, (*b*) VPO(23.1 wt%)/TiO_2–SiO_2, (*c*) VPO(16.7 wt%)/TiO_2–SiO_2, (*d*) VPO(10.2 wt%)/TiO_2–SiO_2, (*e*) VPO(6.7 wt%)/TiO_2–SiO_2, (*f*) VPO(10.2 wt%, 300 °C)/TiO_2–SiO_2, (*g*) TiO_2–SiO_2

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Table 1 Selectivity of the oxidation of propane over VPO/TiO_2–SiO_2 catalysts[a]

Catalyst (VPO loaded amount/wt%)	Catalyst performance				
	Conv./ mol%	Acid Sel.[b]/ mol%	CO_x Sel./ mol%	Acid yield/ mol%	AA/Ac[c]
TiO_2–SiO_2	≈0				
VPO	15	47.2	51.0	7.0	1.12
VPO/TiO_2–SiO_2					
8.2	16.2	51.7	32.0	8.3	1.70
10.7	18.3	55.3	31.4	10.1	1.75
16.7	21.8	61.2	29.0	13.3	1.79
23.1	20.5	44.1	52.8	9.0	1.41

[a] Reaction conditions: GHSV (900 h^{-1}), feed gas ($O_2 : C_3H_8 : H_2O$ = 73.4 : 3.2 : 23.4), T (300 °C). [b] Acids include acrylic acid and acetic acid. [c] AA/Ac: the yield distribution of acrylic acid (AA) and acetic acid (Ac).

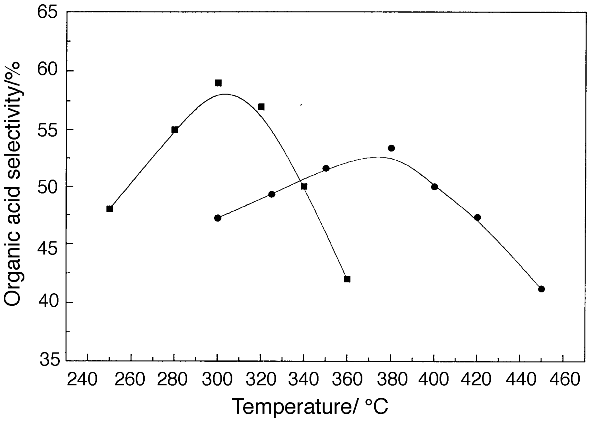

Fig. 2 Effect of temperature on selective oxidation of propane. (■) VPO(16.7 wt%)/TiO_2–SiO_2, (●) VPO. Reaction conditions: GHSV (900 h^{-1}), feed gas ($O_2 : C_3H_8 : H_2O$ = 73.4 : 3.2 : 23.4)

only 51.7% at 380 °C for unsupported catalyst. On the other hand, the lifetime of the supported catalyst is enhanced greatly. No activity decay can be observed after operating several days at lower reaction temperature. This indicates that the coke may be effectively reduced, which is important for use in practice.

It is clear that dispersed VPO/TiO_2–SiO_2 may effectively depress the over-oxidation of propane, which is favorable for improving the selectivity. After the loaded amount of VPO was increased to 16.7 wt%, the catalyst activity changed slightly and the selectivity to acids started to decrease gradually. According to the reappearance of small peaks for VPO in the XRD spectra, bulk VPO may be formed on the TiO_2–SiO_2 surface, which results in more side reactions. It can be suggested that highly dispersed VPO creates new active sites favorable for improving the propane oxidation reaction,[7,8] but a VPO multilayer covering the TiO_2–SiO_2 xerogel surface will lead to deep oxidation of propane at higher temperature.

Generally, supported VPO/TiO_2–SiO_2 catalysts show good performance for selective oxidation of propane, especially at relatively low temperature (300 °C); the experimental results show that highly dispersed VPO can effectively depress side reactions to improve the selectivity, while simultaneously reducing the coking of the catalyst through a decrease of the reaction temperature. There is no doubt that, if further improvements in the activity while maintaining the high selectivity can be made, supported VPO/TiO_2–SiO_2 catalysts will be promising catalysts for the selective oxidation of propane.

Acknowledgements

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