

A Good Performance VPO Catalyst for Partial Oxidation of *n*-Butane to Maleic Anhydride

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A VPO catalyst prepared by the reaction of vanadium pentoxide and isobutyl alcohol/benzyl alcohol in the presence of polyethylene glycol with the molecular weight of 2000 (PEG2000) was found to be highly selective and active for the conversion of *n*-butane to maleic anhydride.

The vanadium phosphorus oxide catalysts (VPO) are widely used for selective oxidation of *n*-butane to maleic anhydride. The typical performance for currently used industrial VPO catalyst was the MA yield of 55–58%, with butane conversion of around 85% and MA selectivity of ca. 65 mol%. The selectivity was not sufficiently high and large amount of butane was burned to CO_x . It is commonly suggested that the efficient catalysts are associated with the presence of vanadyl pyrophosphate, $(\text{VO})_2\text{P}_2\text{O}_7$, and the catalyst performance depends strongly on the preparation history.^{1–3} In one standard method, the catalysts can be prepared by using HCl as the reducing agent, and the obtained catalyst typically had low surface areas (< 10 m^2/g).^{1,3} In another standard procedure, the VPO catalysts with higher surface area (around 20 m^2/g) can be prepared by using alcohols as solvent and reducing agent, and they generally showed better catalytic performance than the former.^{3,4} Since the total surface area is closely related to the active sites available for the reaction, it is a constant interesting project for researchers if some novel methods can be applied to prepare high-surface area VPO catalyst which still maintains the essential active and selective component or phase for the reaction. Different approaches have been tried to prepare small particle, high-surface area system, including mechanical milling⁵ and super critical field drying (SCFD) process⁶ in our laboratory. However, these methods are generally not so easy to operate and control the process, especially for large quantity production. In this work, we first reported here that the VPO catalyst was prepared in the presence of polyethylene glycol. The obtained catalyst showed rather high surface area (41 m^2/g), small particle size (< 100 nm) with rather even particle size distribution and well-crystallized $(\text{VO})_2\text{P}_2\text{O}_7$ phase. The catalytic performance was enhanced notably on the so-obtained sample.

Two catalysts were prepared for comparison: for the VPO1, the preparation procedure was detailed in a Chinese patent.⁷ Typically, 3.2 g of V_2O_5 were suspended in a mixture of 70 mL of isobutyl alcohol and 50 mL of benzyl alcohol under refluxing, then PEG 2000 and H_3PO_4 (85%) were added under further refluxing, with a molar ratio of the repeating unit ($\text{CH}_2\text{CH}_2\text{O}$) of PEG2000 to the vanadium being 2 and the P/V molar ratio being 1.2. The resulting suspension was cooled down to room temperature and filtered. The precipitate was washed with isobutyl alcohol and acetone, and then dried at 393 K for 24 h. The precursor was heated from room temperature to 673 K, at a

rate of 2 K/min, in an atmosphere of 1.5% *n*-butane/air and activated at this temperature for 12 h (GHSV=1800 h^{-1}). For the VPO2, it was prepared in the similar way except that the PEG2000 was not adopted.

The BET surface areas were measured by nitrogen adsorption at 77 K using a Micromeritics ASAP 2000 adsorption apparatus. X-ray diffraction (XRD) was conducted on a Shimadzu D/MAX-RA diffractometer with graphite filtered $\text{Cu K}\alpha$ radiation. XPS was performed on a VG ESCALAB MKII spectrometer, with the X-ray energy of 1253.6 eV ($\text{Mg K}\alpha$). The binding energy was referred to the C1s signal (284.6 eV). Infrared spectra were collected on a Nicolet 170SX Fourier transform infrared spectrometer. The catalyst evaluation was carried out in a quartz micro-reactor and 0.5 g catalyst was charged. The reaction mixture consisted of $n\text{-C}_4\text{H}_{10}/\text{O}_2/\text{N}_2 = 1.5/17.2/81.3$ (volume ratio) with GHSV=1200 h^{-1} . The reaction temperature was in the range of 593–698 K. Two on-line gas chromatography systems were adopted to analyze the outlet reaction mixture.

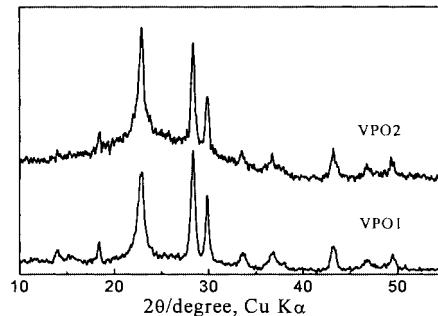


Figure 1. XRD patterns for VPO1 and VPO2.

The BET surface area of VPO1 is 41 m^2/g , much higher than that of VPO2, 19 m^2/g . The XRD results indicated that the two precursors were all the well-crystallized $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ phase. The XRD patterns for both the VPO1 and VPO2 catalysts accords well to those of $(\text{VO})_2\text{P}_2\text{O}_7$ phase,^{1–3} seen in Figure 1. Note that although the major phase composition was almost the same for the two catalysts, the crystallinity and the relative diffraction intensities for different crystal planes are different (for VPO1, $I_{(200)}/I_{(042)} = 0.83$ and $\text{FWHM}_{(200)} = 0.56$; for VPO2, $I_{(200)}/I_{(042)} = 1.14$ and $\text{FWHM}_{(200)} = 0.40$), reflecting the deviations in microstructure between these two samples. The infrared spectra showed that both VPO1 and VPO2 had the characteristic IR features of the vanadyl pyrophosphate,⁸ namely, the bands of 1248 cm^{-1} , 1141 cm^{-1} , 1080 cm^{-1} , and 969 cm^{-1} , but the 1248 cm^{-1} band was rather weak for the VPO2 sample (not shown). The C–H and C–O vibration bands were not observed in the infrared spectrum of the freshly activated

VPO1 sample, suggesting the PEG agent had been removed thoroughly after the activation procedure. The XPS data demonstrated that P element was enriched on the surfaces of these two catalysts, with the surface P/V ratio of 1.6 for VPO1 and 1.5 for VPO2 respectively, and this was in good agreement with the other observation.⁹ The binding energies of V2p_{3/2} (517.2 eV for VPO1 and 516.9 eV for VPO2) and O1s (531.6 eV for VPO1 and 531.2 eV for VPO2) are very close to those of (VO)₂P₂O₇ reported.⁹

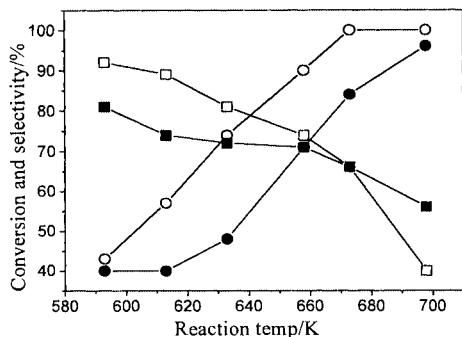


Figure 2. Temperature courses of *n*-butane oxidation over VPO1 (open) and VPO2 (solid) catalysts: (○) conversion, (□) selectivity.

The catalytic performances of these two catalysts are shown in Figures 2 and 3. In the temperature range of 593–698 K, the selectivity of maleic anhydride (MA) on the VPO1 catalyst was decreased more notably than that on VPO2, while the conversion of *n*-butane on VPO1 was increased drastically with increasing temperature. At rather low reaction temperature, that is, 593 K, the catalyst VPO1 showed only 43% of conversion and 92 mol% of selectivity. The catalyst showed its best performance at 658 K: the conversion of 90% with the MA selectivity of 74 mol%, resulting in the MA yield of 67 mol%. Comparatively, only 50 mol% MA yield was obtained on the VPO2 at the same temperature, with the conversion of 71% and the selectivity of 71 mol%. At the typical reaction temperature, namely, 673 K, the VPO2 catalyst showed its best performance: the conversion of 84% and the MA selectivity of 66 mol%, yielding 55 mol% MA. Note that on the former catalyst, even the reaction temperature is 15 K lower, the performance so obtained is considerably better than that of the latter obtained at 673 K. As shown in Figure 3, both VPO1 and VPO2 catalysts become less selective with increasing conversion, but the former showed a faster drop in selectivity in the conversion range of 40–90%.

The use of PEG in preparation seems to provide an easy and effective media to generate high surface area VPO catalyst. The presence of PEG could decrease the surface energy of nucleation of precursor particles, and the adsorbed PEG on the freshly formed precursor surfaces can effectively hinder the agglomeration of the precursor particles. The gradual removal

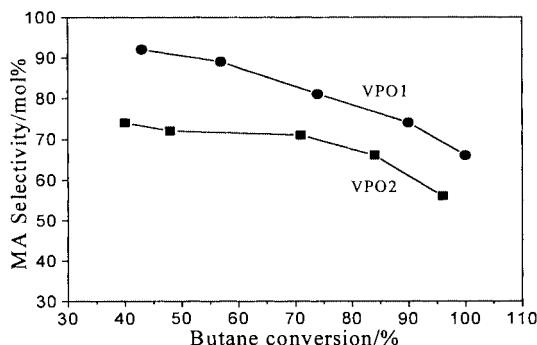


Figure 3. Selectivity of the VPO1 and VPO2 catalysts as a function of the conversion of *n*-butane.

of PEG in the activation procedure is also beneficial in generating the high surface area sample. This kind of catalyst appears more active and selective than that prepared in a normal route without PEG. This could be due to the more available active sites for MA formation per mass of catalyst (as revealed by its significantly higher surface area) and its unique structural feature or morphology (partly evidenced by XRD and FT-IR results as mentioned above). Thus the method developed in this study generates a more environmentally friendly and productive VPO catalyst for partial oxidation of *n*-butane to MA. Another interesting feature of the PEG treated sample is its good low-temperature performance. At 633 K, the MA yield can reach 60 mol%, however, the catalyst prepared without PEG showed much lower performance at the same temperature, seen in Figure 2.

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