Applied Catalysis A: General 341 (2008) 70–76

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Water modification of PEG-derived VPO for the partial oxidation of propane

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ARTICLE INFO

Article history:
Received 7 September 2007
Received in revised form 13 February 2008
Accepted 16 February 2008
Available online 23 February 2008

Keywords:
Vanadium phosphorus oxide
Propane
n-Butane
Oxidation
Acrylic acid
Maleic anhydride

ABSTRACT

In this study, the PEG-derived VPO precursors were subject to water refluxing (90 °C, 8 h) and *in situ* activation in a steam-containing environment. For comparison, the VPO precursors without water refluxing were also activated in a similar manner. The IR measurement indicated that the majority of PEG in the precursor has been removed during water refluxing, and the VPO is essentially unenwrapped by PEG. The consequence is an increase of particle size and crystallinity of VPO as well as decreases in surface acidity and site density. The activation of catalysts in a stream-containing environment has an influence on the content of V^{5+} species and on the reduction behavior of the VPO catalysts. The VPO catalyst activated with 20% water vapor (by volume) in the feed shows the highest crystallinity. Compared with the non-PEG-derived VPO precursor, the PEG-derived one undergoes structure changes of higher severity during the water/steam treatments. The VPO catalyst generated from the PEG-derived precursor with water refluxing and activated with steam (20%) exhibited a propane conversion of 25% and a (AA + HAc) selectivity of ~70%. The superior catalyst behavior can be interpreted in terms of the higher crystallinity of the $(VO)_2P_2O_7$ phase, the lower content of V^{5+} species, and the milder surface acidity as caused by the water/steam treatments.

1. Introduction

Due to economic and environmental considerations, the partial oxidation of light alkanes (C_1–C_5) to olefins and oxygenates (e.g. alcohols, aldehydes, anhydrides and acids) has been widely studied [1]. Vanadium phosphorus oxide (VPO) is a commercially produced catalyst for the partial oxidation of *n*-butane to maleic anhydride (MA). The catalytic system is rather complicated and many efforts [2–12] have been made to advance our understanding of the nature of the catalysts.

Vanadyl pyrophosphate [$(VO)_2P_2O_7$] can be obtained via the dehydration of vanadyl phosphate hemihydrate ($VOHPO_4 \cdot 0.5H_2O$) precursor. However, it is known that the history of preparation can have a strong influence on catalyst properties, including phase composition, morphology, particle size, and surface P/V ratio [2,3]. Certain synthesis routes can result in unique $(VO)_2P_2O_7$ that shows obvious discrepancies in characteristics and catalytic performance [4–7]. Besides being efficient in the oxidation of *n*-butane to MA, the VPO catalysts have been found active in propane partial oxidation to acrylic acid (AA) [13–24]. The results of Ai [14–16] and Landi et al. [22–24] on the VPOs of different P/V ratios revealed that changes in VPO phase composition have significant effects on catalytic behavior of this kind of catalyst. It has been observed that the V^{5+}-containing phases play an important role in the partial oxidation of *n*-butane to MA [5–7,25–28]. However, little is known about the functionality of V^{5+}-containing phases in the partial oxidation of propane to AA. Landi et al. studied the effect of water on the character and reaction performance of conventionally prepared VPO catalysts for propane partial oxidation to acrylic acid [22–24]. In this work, we treated the PEG-derived VPO precursors by means of water refluxing and stream activation and investigated the influences of such treatments on the characteristics and behaviors of the catalysts.

2. Experimental

2.1. Preparation of catalyst precursor

The precursor of VPO catalyst was prepared according to the procedures reported elsewhere [28]. Briefly, V_2O_5 (3.2 g) was added into a mixed solution of *iso*-butanol/benzyl alcohol (in 1/1 volume ratio). The suspension was heated to 140 °C and refluxed for 4 h under the protection of N_2 atmosphere. After that, 10 ml *iso*-butanol was added, and 1 h later, 15 ml benzyl alcohol and 1.5 g PEG surfactant ($M_W = 6000$) were added under stirring. The mixture was left standing for 1 h prior to the addition of H_3PO_4 (85%, to reach a P/V atomic ratio of 1.1). The so-obtained

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doi:10.1016/j.apcata.2008.02.029

suspension was subject to 4 h of reflux during which there was a color change from nearly black to light blue. The solid was then separated from the liquid by filtration and washed three times with *iso*-butanol and ethanol. The resulting solid was then subject to a water treatment process, namely, refluxing in hot water (90 °C) for 8 h. The solid was recovered by filtration, and dried in air at 120 °C for 24 h. The blue $VOHPO_4 \cdot 0.5H_2O$ so obtained is the "PEG-derived and water-treated" VPO precursor (denoted as PW hereinafter). The PEG-derived precursor without undergoing the water-refluxing process is denoted as PNW.

2.2. Catalyst activation

In order to transform PW into an active VPO catalyst, the precursor was subject to activation in a fixed-bed micro-reactor under a flow (gas hourly space velocity (GHSV = 1250 ml g_{cat}^{-1} h^{-1}) of propane, oxygen and helium (v/v/v = 2.2/15.5/82.3) at 430 °C. After a period of approximately 17 h, the temperature was lowered to 400 °C, and water vapor was introduced (partial pressure varied from 0 MPa to 0.04 MPa; regulated by using a water saturator controlled at different temperatures) into the feed. For each partial pressure of water vapor, the PW sample was kept in the feed for about 20 h. The VPO catalysts that resulted from the PW activation with 0%, 10%, 20%, 30%, and 40% (by volume) of water vapor will be denoted as CW0, CW10, CW20, CW30, and CW40, respectively, hereinafter. For comparison purposes, portions of PNW were activated similarly and will be denoted as CNW0, CNW10, CNW20, CNW30, and CNW40, respectively, hereinafter.

2.3. Catalyst evaluation

The catalytic reactions were carried out in a fixed-bed micro-reactor; and the procedures were similar to those reported elsewhere [28,29]. To achieve reasonable levels of conversion and selectivity for propane oxidation, we evaluated the samples at a GHSV of 900–1500 ml h^{-1} g_{cat}^{-1}.

2.4. Catalyst characterization

Scanning electron microscopy (SEM) was performed over an X650 microscope (Jarrel-Ash Co., USA). The magnification was in the range of 2000–5000. X-ray powder diffraction (XRD) was conducted on an X'Pert Pro diffractrometer using Cu Kα radiation at operating parameters of 5–35 kV and 5–15 mA, and the patterns were acquired within a 2θ range of 10–80°. Raman spectra were recorded at RT on a LABRAM-HR Raman spectrometer (laser source: 514.3 nm; power: 1.0–1.5 mW). H_2 temperature-programmed reduction (H_2-TPR) was performed from RT to 800 °C at a rate of 5 °C min^{-1} in a flow of 5% H_2/N_2 (v/v; flow rate = 40 ml min^{-1}) and isothermally held at 800 °C until reduction was complete. NH_3-calorimetric measurements were performed on a Tian-Calvet heat-flux apparatus; the sample was degassed at 300 °C for 1 h before exposure to ammonia.

3. Results and discussion

3.1. SEM

Fig. 1 shows the typical SEM images of PW and CW20. There is no detection of the "rose-like" morphology that is common among VPOs prepared conventionally in organic media [23,24]. Instead, both PW and CW20 samples exhibit plates and blocks in dimension of micrometers (Fig. 1). This is not surprising because during activation the transformation of PW to CW20 is thought to be topotactic. The unique morphology of PW is likely to be a result of adding PEG in the catalyst preparation. The presence of PEG in the synthesis medium would lower interfacial surface energy, and consequently there is the generation of fine particles as a result of uniform nucleation [28]. Landi et al. reported that the grain size of a water-treated VPO is significantly bigger than that of a non-treated one [22]. The PEG material is soluble in water. In the present study, the PEG-derived VPO precursor was subject to water refluxing at 90 °C for 8 h before activation (at 703 K for 17 h). The results of IR investigation (not shown) conducted after water refluxing confirmed that most of the PEGs in VPO precursor had been removed. One should note that, in the case of Ref. [28], the treatment of water refluxing was not applied before catalyst activation, and in fact most of the residual PEGs were removed during catalyst activation (673 K for 15 h). In other words, the way adopted for PEGs removal in the present study is different from that reported in Ref. [28]. Water refluxing of VPO precursor leads to significant aggregation of VPO precursor and as a result larger VPO particles after activation. Such a deduction is supported by the XRD results described in the following section.

3.2. XRD

The XRD patterns of CW0–CW40 are shown in Fig. 2. The diffraction lines at 2θ = 23°, 28.4°, and 29.8° observed over the CW0–CW40 samples are typical of the $(VO)_2P_2O_7$ phase, and are assigned to (2 0 0), (0 2 4), and (032) diffraction, respectively [30]. Compared with CW0, the CW10–CW40 samples show notably higher diffraction intensity, and among all of the samples, CW20

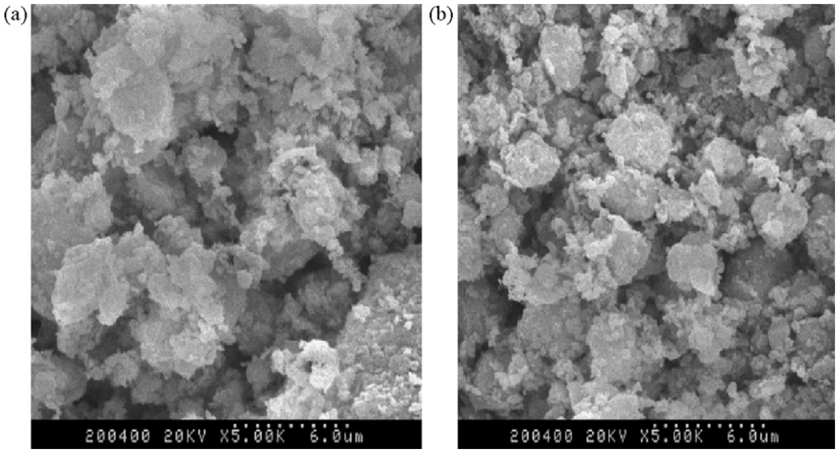

Fig. 1. SEM images of (a) PW and (b) CW20.