The Effect of Using H₄P₂O₇ as Phosphorus Source for Synthesizing Vanadyl Pyrophosphate Catalysts

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Abstract

Vanadyl pyrophosphate (VO)₂P₂O₇ catalysts synthesized via VOPO₄·2H₂O were investigated by using BET surface area measurement, X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Temperature-Programmed Techniques (TPD and TPRS). H₃PO₄ and H₄P₂O₇ were used as the phosphorus source. Only pyrophosphate phase was observed for both final catalysts after 75 hours of calcination in a reaction flow of n-butane/air mixture (0.75% n-butane/air). However, catalyst derived from H₃P₂O₇ based preparation (denoted VPD ortho) exhibit better crystallinity and slightly higher BET surface area compared to the H₄P₂O₇ based preparation (denoted VPD pyro). The nature of the oxidants for both catalysts was investigated by O₂-TPD. For VPD pyro, TPD showed an oxygen peak maximum at 986 K and a shoulder at 1003 K, whereas for VPD ortho, the oxygen was desorbed as two peaks maxima at 966 and 994 K. The total amount of oxygen desorbed thermally from VPD pyro (3.60×10²⁰ atom·g⁻¹) is higher than that obtained for VPD ortho (3.07×10²⁰ atom·g⁻¹). VPD pyro displayed a slightly improved activity and selectivity for n-butane oxidation. A proper amount of V⁵⁺ species may have an effect on the enhancement of the catalytic activity.

Introduction

Vanadyl pyrophosphate, (VO)₂P₂O₇ catalysts currently are the most active phase to transform the only alkane used commercially in selective oxidation process from n-butane to maleic anhydride (MA). Maleic anhydride is an important material for manufacturing unsaturated polyester resins, agricultural chemical, food additives, lubricating oil additives and pharmaceuticals [1].

Most of the studies reported that (VO)₂P₂O₇ was obtained from the precursor VOHPO₄·0.5H₂O by calcination in a reaction condition at 673 K. This precursor played an important role in the transformation of the final catalyst [2]. Preparation of the precursor is the key to obtain a high performance catalyst [3,4,5,6]. The phosphorus sources employed for the synthesis of VOHPO₄·0.5H₂O also reported to give a strong influence in the synthesis of vanadium phosphate catalysts [3].

The purpose of this paper is to investigate the physico-chemical properties of the vanadyl pyrophosphate, (VO)₂P₂O₇ catalyst prepared by using two different sources of phosphorus i.e.: H₃PO₄ and H₄P₂O₇. The catalytic activity of these catalysts will also be reported.

Experimental

Catalysts Preparation

Via VOPO₄·2H₂O and H₄P₂O₇

V₂O₅ (15.0 g) and H₄P₂O₇ (69.9 g) mixture was refluxed in water for 4 hours. Then the resulting mixture (yellowish coloured) was recovered by centrifuged, following by filtration and washed with cold water. The solid obtained was then dried in air for 24 hours at 373 K and confirmed by XRD as VOPO₄·2H₂O. This material was refluxed with isobutanol for 16 hours to obtain VOHPO₄·0.5H₂O precursor (denoted Pyro ortho).

Via VOPO₄·2H₂O and H₃PO₄

VOPO₄·2H₂O was prepared by mixing V₂O₅ (15.0 g) with H₃PO₄ (90 mL). This mixture was refluxed in water for 16 hours. Then the resulting mixture (yellowish coloured) was recovered by filtration and...
washed with cold water and dried in air for 24 hours at 373 K. VOPO₄·2H₂O was then refluxed with isobutanol for 16 hours to obtain the VOHPO₄·0.5H₂O precursor (denoted as Orthopre).

These resulting precursors were then calcined in a flow of n-butane/air mixture (0.75% n-butane in air) for 75 hours at 673 K. The final catalysts were denoted VPD_{pyro} (using H₄P₂O₇) and VPD_{ortho} (using H₃PO₄).

**Catalysts Characterization**

The BET surface areas of the catalysts were measured by using nitrogen adsorption at 77 K. This was done by using ThermoFinnigan Sorptomatic Instrument model 1990.

The bulk average oxidation states of vanadium in the catalysts were determined by redox titration following the method of Niwa and Murakawi [7].

The X-ray diffraction (XRD) analyses were carried out using a Shimadzu diffractometer model XRD 6000 employing Cu Kα radiation to generate diffraction patterns from powder crystalline samples at ambient temperature.

SEM was done using a Quanta 200 ESEM FEG electron microscope.

Temperature Programmed Desorption (TPD) of O₂ analysis was done by using a ThermoFinnigan TPDRO 1110 apparatus utilizing a thermal conductivity detector (TCD).

Temperature Programmed Reaction Spectroscopy (TPRS) profile was obtained by passing an n-butane/He stream (2.0%, 101 kPa, 25 cm³/min) over the catalyst (0.5 g) and raising the temperature from ambient to 1173 K at 5 K/min. This was done by using ThermoFinnigan TPDRO 1100 apparatus connected via a heated capillary to a quadrupole MS (Pfeiffer).

**Results and Discussion**

**BET surface area measurement and redox titration**

The BET surface area for VPD_{ortho} and VPD_{pyro} are 23.18 and 25.40 m²/g, respectively. These values are higher compared to 12.0 m²/g as reported by Bartley _et al._ [3]. The average oxidation numbers of vanadium for both catalysts are given in Table 1. By using H₃PO₄ as the phosphorus source was found to decrease the average oxidation number from 4.26 to 4.18 _i.e._ a reduction of V⁵⁺ oxidation state from 26 to only 18%. This observation is similar to those reported by Bartley _et al._ [3].

**Table 1**

| Catalysts  | Specific surface area, (m²/g) | V⁴⁺ (%) | V⁵⁺ (%) | Average oxidation state |
|------------|------------------------------|---------|---------|------------------------|
| VPD_{ortho}| 23.18                        | 74      | 26      | 4.26                   |
| VPD_{pyro}| 25.40                        | 82      | 18      | 4.18                   |

**X-ray Diffraction**

The XRD pattern of the precursor, Orthopre (Fig. 1) showed the characteristic peaks that matched perfectly with VOHPO₄·0.5H₂O with peaks appeared at 2θ = 15.6°, 27.0° and 30.4° which correspond to (001), (121) and (220) reflections, respectively. However, the usage of H₄P₂O₇ leads to the domination of reflection at 2θ = 30° which indexed to the (220) plane. This observation is similar to the previous report [3].

Fig. 1. XRD patterns of Orthopre and Pyropre.

The XRD patterns for VPD_{ortho} and VPD_{pyro} catalysts shown in Fig. 2 were matched perfectly with the patterns of a pyrophosphate phase. The main peaks observed at 2θ = 23.0°, 28.5° and 29.9° which correspond to (020), (204) and (221) planes, respectively are more intense for the catalyst derived from H₄P₂O₇ compared to the catalyst prepared using H₃PO₄.
Table 2 shows the line width of the (020) and (204) plane reflections. The parameter used to determine the crystallite size is the half width of the (020) peak. The line width increases with the decreasing size of the crystallite. The particle size of VPDortho at (020) and (204) were calculated by using Debye-Scherrer equation [8] as 151.9 and 97.7 Å, respectively. However, the particle size for VPDpyro catalyst was decreased to 105.3 and 55.8 Å, respectively.

Table 2

| Catalysts | Line width (020), Å | Line width (204), Å | Thickness (020), Å | Thickness (204), Å |
|-----------|---------------------|---------------------|-------------------|-------------------|
| VPDortho  | 0.5400              | 0.8280              | 151.9             | 97.7              |
| VPDpyro   | 0.7809              | 1.4533              | 105.3             | 55.8              |

Scanning Electron Microscope

The surface morphologies of VPDortho and VPDpyro are shown in Fig. 3. Both catalysts show a platelets structure which closely packed together forming a rosette-shape cluster. VPDortho showed a rosette type structure with a crystallite of uniformed sized however VPDpyro catalyst showed an improper arrangement of rosette cluster with more isolated platelet.

Temperature-Programmed Desorption of Oxygen

The oxygen desorption spectra shown in Fig. 4 were obtained by pretreating the catalyst by heating them to 673 K in oxygen flow (1 bar, 25 cm³×min⁻¹), holding them under that stream for 1 hour before cooling them to ambient temperature. Then the flow was switched to helium and the temperature was raised to 1173 K following the conductivity of oxygen by a thermal conductivity detector (TCD). VPDortho gave two overlapped peaks at 966 and 994 K, whereas VPDpyro also gave two desorption peaks maxima at 986 and 1003 K. There are no desorption peaks for oxygen in the temperature range from 300 to 850 K which correspond to the specific site for chemisorbed molecular oxygen. The total amount of oxygen desorbed from the VPDortho is 3.07×10²⁰ atom×g⁻¹ (Table 3). The usage of H₃P₂O₇ slightly increased the amount to 3.62×10²⁰ atom×g⁻¹ i.e., an increment of ~15% of the total oxygen desorbed for VPDpyro. These are the lattice oxygen which also has been observed earlier and showed 100% selectivity towards partial oxidation of C₄ hydrocarbons [9].
Both samples exhibit catalytic activity with the production of intermediates for \(n\)-butane selective oxidation to maleic anhydride (MA), i.e., butene, butadiene and furan. The temperature profiles of Fig. 5 indicate that by replacement of \(\text{H}_3\text{PO}_4\) to \(\text{H}_4\text{P}_2\text{O}_7\), exhibit minimal influence on the evolution of the catalytic function. \(\text{VPD}_{\text{ortho}}\) developed activity at 674 K (as shown in the onset of furan production in Fig. 6) whereas \(\text{VPD}_{\text{pyro}}\) requires a lower temperature at 588 K. A higher rate of butene production and a lower temperature peak maximum of butene (Fig. 5) shows that \(\text{VPD}_{\text{pyro}}\) gave higher activity as compared to \(\text{VPD}_{\text{ortho}}\). This is in agreement with the earlier finding [3]. Total amount of selective products for both catalysts as shown in Table 4 indicate that \(\text{VPD}_{\text{pyro}}\) has a better selectivity.

The most significant observation in the present study is that furan was observed as one of the intermediate products.
Intermediate found for this anaerobic partial oxidation of \( n \)-butane. This was not observed previously by using the same catalyst prepared using "classical" organic method [10]. The total amounts of CO\(_2\) produced by these two catalysts are similar. However VPD\(_{\text{ortho}}\) produced higher amount (24% more) of CO\(_2\) at lower temperature peak (783 K) as compared to VPD\(_{\text{pyro}}\).

**Table 4**  
Percentage of selective and unselective products

| Catalysts | But-1-ene | But-1,3-diene | CO   | CO\(_2\) | Furan |
|-----------|-----------|---------------|------|----------|-------|
| VPD\(_{\text{ortho}}\) | 25.4% | 6.08% | 66.2% | 1.90% | 0.62% |
| VPD\(_{\text{pyro}}\) | 25.4% | 6.87% | 63.9% | 1.90% | 0.98% |

Fig. 5. Production of butene, butadiene, CO\(_2\) by TPRS over the VPD\(_{\text{ortho}}\) and VPD\(_{\text{pyro}}\).

Fig. 6. Production of furan by TPRS of \( n \)-butane over the VPD\(_{\text{ortho}}\) and VPD\(_{\text{pyro}}\).
VPD$_{pyro}$ which may due to the increment of the V$^{5+}$ oxidation state in the catalyst. Previous study has shown that the presence of V$^{5+}$ phases can decrease the catalytic performances [11,12]. However, according to Abon et al. [13], the existence of V$^{5+}$ sites in the catalyst leads to the enhanced catalytic performances for $n$-butane oxidation. The vanadium oxidation state of VPD$_{pyro}$ in this study is 4.18 indicates that the presence of a small amount of V$^{5+}$ is essential for a higher selectivity.

**Conclusions**

The effect of using H$_4$P$_2$O$_7$ in replacement of H$_3$PO$_4$ in the synthesised of (VO)$_2$P$_2$O$_7$ are:

- A decreased of vanadium oxidation state from 4.26 to 4.18.
- An increasing of the lattice oxygen desorbed thermally.
- The morphology of VPD$_{pyro}$ showed the increasing of isolated platelet for each rosette shape clusters.
- Higher activity and selectivity obtained from $n$-butane oxidation.

**References**

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