

# Effects of mechanochemical treatment to the vanadium phosphate catalysts derived from $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$

Y.H. Taufiq-Yap<sup>a,\*</sup>, C.K. Goh<sup>a</sup>, G.J. Hutchings<sup>b</sup>, N. Dummer<sup>b</sup>, J.K. Bartley<sup>b</sup>

<sup>a</sup> Department of Chemistry, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

<sup>b</sup> School of Chemistry, Cardiff University, P.O. Box 912, Cardiff CF10 3TB, UK

Received 18 January 2006; received in revised form 22 May 2006; accepted 27 June 2006

Available online 8 August 2006

## Abstract

Modification by using mechanochemical treatment of vanadium phosphate catalysts on the microstructure, morphology, oxygen nature and catalytic performance for *n*-butane oxidation is described and discussed. In this work, the precursor,  $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$  prepared by reduction of  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  by isobutyl alcohol was subjected to a high energy planetary ball mill for 30, 60 and 120 min in ethanol. The ball milling process reduced the crystallite size of the catalysts and consequently increased their surface area. The morphologies of the milled catalysts are dependent on milling time. The highest reactivity and mobility of the lattice oxygen species has been achieved by the catalyst milled for 60 min with lower reduction peak temperature and higher amount of oxygen atoms removed. The oxygen species removed from the active  $\text{V}^{4+}$  phase was shown to be correlated with the rate of reaction. A good relationship was also found between the oxygen species associated with  $\text{V}^{5+}$  and maleic anhydride selectivity. However, a larger amount of this oxygen species will give a deleterious effect on the conversion rate. The present study demonstrate that the mechanochemical method (with an appropriate duration) effectively enhanced the catalytic activity by increasing the surface area and controlling the reactivity, and that the amount of oxygen species contributed to the partial oxidation of *n*-butane to maleic anhydride.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Vanadium phosphate; Mechanochemical; *n*-Butane oxidation; Maleic anhydride

## 1. Introduction

Vanadium phosphate (VPO) catalysts represent the sole example of an industrial catalyst for the selective oxidation of *n*-butane to maleic anhydride (MA). It is known that the catalytic performance of vanadium phosphates depends on the history of preparation of the catalyst precursor,  $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$  [1,2]. Typically, the active catalyst consists  $(\text{VO})_2\text{P}_2\text{O}_7$  in combination with some  $\text{V}^{5+}$  phosphate and the topotactically transformation to final catalyst [3]. Hence, controlling the physicochemical properties of the precursor is an important factor in determining the physicochemical properties and the performance of the eventual catalyst following activation. In general,  $\text{V}_2\text{O}_5$  is used as a source of vanadium, and  $\text{H}_3\text{PO}_4$  is used as a source of phosphorus. Hence, a reducing agent is required to synthesise the  $\text{V}^{4+}$  precursor phase and a broad range

of reducing agents and solvents have been used [4,5]. Initial catalyst preparations [2,4] used water as solvent but most studies, in recent years, have concentrated on the use of alcohols since they can exhibit the dual role of solvent and a reducing agent. Hutchings et al. [6–8] have shown that very active catalysts can be prepared using a two-stage method based on  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ . In particular, they have found that the alcohol used in the second step to reduce the  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  to  $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$  can produce catalyst precursors with better morphology and texture.

Mechanochemical method has been employed in the modification of morphology and texture of the catalyst precursor to improve the catalytic performance of the vanadium phosphate catalyst [9–17]. Zazhigalov et al. [13] reported that the ball milling process could reduce the particle size of catalysts and corresponding increase in the specific surface area. This observation was agreed by Fait et al. [14] who also reported that a decreased particle size and an increased microstrain in the  $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$  precursor would improve the catalytic properties of the V–P–O catalysts. In another report by Hutchings and Higgins [15] on the precursor  $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$  milled in

\* Corresponding author. Tel.: +603 8946 6809; fax: +603 8946 6758.  
E-mail address: [yap@fsas.upm.edu.my](mailto:yap@fsas.upm.edu.my) (Y.H. Taufiq-Yap).

the presence of cyclohexane as solvent and dispersants based on poly-12-hydroxystearic acid, they observed a significant reduction of particle size of the  $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$  ( $5\text{--}0.035\ \mu\text{m}$ ) that gave final catalysts with high surface area following activation ( $>40\ \text{m}^2\ \text{g}^{-1}$  versus  $9\ \text{m}^2\ \text{g}^{-1}$  without ball milling). They also found that these catalysts are particularly active under fuel rich reaction conditions, when high MA yields can be obtained. Ayub et al. [16] found that Bi-promoted vanadyl pyrophosphate milled in air for relatively short times (5 min) could generate a material that was amorphous in powder X-ray diffraction. They also observed that the blossom secondary morphology of the catalyst was lost under ball milling process. Although they further noted that the ball milling process could increase the specific surface area, the yield and conversion per unit surface area were decreased. Hence, the full benefits that could be expected from the enhanced surface area are unfortunately not produced. Wang et al. [17] showed that the ball milling process broadened the major powder X-ray diffraction peaks, indicating that both a reduction of particle size and a fine variation in local structure could occur in the milled solids, consequently leading to the improvement of catalytic performance of the VPO catalysts.

The purpose of this study is to employ the mechanochemical pretreatment for morphological and textural modification of vanadium phosphate catalysts synthesised via reduction of the  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  phase. The structure-activity relationships and the nature and the role of lattice oxygen species of the catalysts are discussed.

## 2. Experimental

### 2.1. Catalysts preparation

The  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  material was prepared by reacting  $\text{V}_2\text{O}_5$  (30.0 g from Fluka) with  $\text{H}_3\text{PO}_4$  ( $144\ \text{cm}^3$ , 85% from Merck) in water ( $720\ \text{cm}^3$ ) under reflux with continuous stirring for 24 h. The yellow solid was then recovered by filtration, washed with distilled water ( $100\ \text{cm}^3$ ) and followed by acetone ( $100\ \text{cm}^3$ ). It was dried at 383 K for overnight. The  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  phase was then confirmed by XRD analysis. After that, the synthesised  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$  (40.0 g) was suspended by rapid stirring into isobutyl alcohol ( $800\ \text{cm}^3$ ) and the mixture was refluxed for 21 h with continuous stirring. A blue solid was recovered by filtration and washed with distilled water ( $100\ \text{cm}^3$ ) followed by acetone ( $100\ \text{cm}^3$ ). The resulting blue solid was further treated in refluxing water (24 ml  $\text{H}_2\text{O}/\text{g}$  solid) for 3 h to remove  $\text{VO}(\text{H}_2\text{PO}_4)_2$  and was separated by filtration and dried overnight in air at 385 K. Mechanochemical pretreatment of the precursor was carried out by using a high energy planetary ball mill (model Pulverisette 4 from Fritsch) with an agate bowl having 250 ml volume together with fifty 10 mm diameter agate balls. About 18 g of the  $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$  and ethanol as solvent were put together inside the bowl. The bowl spins around its own axis and around a second axis outside its centre at 1400 rpm for 30, 60 and 120 min. The resulting unmilled and milled precursors then undergone calcination in a flow of *n*-butane/air mixture (0.75% *n*-butane in air) for 75 h at 673 K to generate the active catalysts,  $(\text{VO})_2\text{P}_2\text{O}_7$ .

### 2.2. Catalysts characterisation

Brunauer–Emmett–Teller (BET) surface area measurements were carried out by using nitrogen adsorption–desorption at 77 K using a ThermoFinnigan Sorptomatic 1990 instrument.

The bulk chemical composition was determined by using a sequential scanning inductively coupled plasma-atomic emission spectrometer (ICP-AES) Perkin-Elmer Emission Spectrometer Model Plasma 1000.

The average oxidation states of vanadium in all the samples were determined by the method described by Niwa and Murakami [18].

X-ray diffraction (XRD) patterns were obtained using a Shimadzu diffractometer model XRD-6000 employing  $\text{Cu K}\alpha$  radiation generated by a Phillips glass diffraction X-ray tube broad focus 2.7 kW type on the catalysts at ambient temperature.

Scanning electron microscopy (SEM) analyses were carried out using a JEOL JSM-6400 electron microscope.

Temperature-programmed reduction ( $\text{H}_2$ -TPR) in  $\text{H}_2/\text{Ar}$  experiment was performed using a ThermoFinnigan TPDRO 1100 apparatus provided with a thermal conductivity detector. The  $\text{H}_2$ -TPR analysis of fresh catalysts was done in  $\text{H}_2/\text{Ar}$  stream (5%  $\text{H}_2$ , 1 bar,  $25\ \text{cm}^3\ \text{min}^{-1}$ ) with raising the temperature from ambient to 1173 K at  $5\ \text{K}\ \text{min}^{-1}$ .

### 2.3. Catalyst testing

The oxidation of *n*-butane to MA was carried out in a fixed-bed microreactor with a standard mass of catalyst (250 mg). The gases *n*-butane and air were fed to the reactor via calibrated mass flow controllers to give a feedstock composition of 1.5% *n*-butane in air. The products were then fed via heated lines to an on-line gas chromatograph for analysis. The reactor comprised of a stainless steel tube with the catalyst held in place by plugs of quartz wool. A thermocouple was located in the centre of the catalyst bed and temperature control was typically  $\pm 1\ ^\circ\text{C}$ . Carbon mass balances of  $\geq 96\%$  were typically observed.

## 3. Results and discussion

### 3.1. BET surface area and chemical analysis

Table 1 shows the effect of the ball milling on the ratio of P/V, BET surface area, oxidation state of vanadium as well as percentage of  $\text{V}^{4+}$  and  $\text{V}^{5+}$  present in the catalysts. It is found

Table 1  
Bulk composition, surface area, average oxidation states and percentage of  $\text{V}^{4+}$  and  $\text{V}^{5+}$  oxidation states present in catalysts

Milling time (min)	P/V (ICP)	Surface area ( $\text{m}^2\ \text{g}^{-1}$ )	Oxidation state of vanadium		
			$\text{V}^{4+}$ (%)	$\text{V}^{5+}$ (%)	Average
0	1.00	16	79	21	4.21
30	0.99	19	69	31	4.31
60	0.99	25	84	16	4.16
120	1.00	15	78	22	4.22

Download English Version:

<https://daneshyari.com/en/article/68323>

Download Persian Version:

<https://daneshyari.com/article/68323>

[Daneshyari.com](https://daneshyari.com)