

Characterization of Mn-Doped Vanadium Phosphorus Oxide (VPO) Catalyst: Effect of Ball Milling

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Abstract

The effect of ball milling on the structure and surface reactivity of the Mn-doped vanadium phosphorus oxide (V–P–O) catalyst is discussed. Mn-doped $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ precursor was prepared via organic method. The precursor was ball milled in isopropyl alcohol using agate balls for 60 min at 800 rpm. XRD, BET surface area measurements, SEM, O_2 -TPD, H_2 -TPR and TPD of NH_3 were used to characterize properties of the final catalysts. The results revealed that mechanical treatment of Mn-doped V–P–O catalyst increased surface area as well as reduced particle size of the material. Furthermore, process also increased exposure of (001) crystallographic plane of $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ precursor. The secondary structure of the milled material is also lost. The total amount of oxygen desorbed (from O_2 -TPD) and removed (by H_2 -TPR) from milled material is higher compared to the unmilled one. The surface acidity of the catalyst was also increased after milling process, as evidenced by lower desorption temperature and higher total amount of the ammonia desorbed.

Introduction

It is well known that the vanadium phosphorus oxide (V–P–O) is the only catalysts commercially used for the partial oxidation of *n*-butane to maleic anhydride (MA) [1]. The active phase is $(\text{VO})_2\text{P}_2\text{O}_7$ and obtained by activating the $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ precursor in a flow of *n*-butane/air mixture at ~ 673 K [1-4]. Generally, physical and chemical properties of the V–P–O catalyst is varied with the conditions of the preparation that determine the texture, particle size, surface area, type of crystal faces exposed and mobility of the lattice of oxygen [1,3]. Brutovský and Geraj [5] investigated catalytic behaviour of a series of promoters such as Li, Ba, Mn, Fe, Co, Ni, Cu, Zn, Pd, Cd, Sn and Ce which are incorporated into the lattice of V–P–O catalysts. Each catalyst had P/V ratio of 1.2 and was prepared by reaction of V_2O_5 with H_3PO_4 in aqueous solution of HCl containing the promoter in the form of salt with non-oxidized anion. They found that the Mn-promoted V–P–O catalyst gave higher maleic anhydride selectivity as compared to either unpromoted or other metals promoted V–P–O catalysts.

Recently, mechanochemical treatment has been suggested to improve physico-chemical and catalytic performance of V–P–O catalyst [6]. Most efficient mechanochemical treatment of the solids can be achieved by using planetary ball mill [7]. Zazhigalov *et al.* [8] reported that mechanochemical treatment could cause repeated fracture of the solids, reducing its particle size and corresponding increase of the specific area. This observation was agreed by Fait *et al.*, [9] which also reported that a decreased particle size and increased of microstrain in the $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ precursor would improved catalytic properties of the V–P–O catalysts. Ji *et al.* [10] have prepared V–P–O catalysts doped by combined components (Zn+Zr+Mo, Zr+Zn and Zr+Mo) through impregnation and then followed by ball milling process. They found that catalyst modified with combination of Zr, Mo and Zn elements and subjected to ball milling process showed increased in the surface area of both precursor and final catalyst. They also reported that ball milling process was able to increase conversion of *n*-butane without sacrificing MA selectivity. Ayub *et al.* [11] reported that the ball milled Bi-promoted $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ in ethanol for 5 min, reduced particle size but did not change phase composition, whereas milling in air for 28 min resulted in amorphous phase and increasing of the mechani-

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cally treated to 30 min led to the formation of $(VO)_2P_2O_7$ phase. They also pointed that ball milling process could increase specific surface area and enhanced activity and selectivity of the *n*-butane to MA. However, they found that ball milling destroyed crystallinity and decreased conversion of *n*-butane and yield of MA per unit surface area.

In this work, Mn-doped $VOHPO_4 \cdot \frac{1}{2}H_2O$ precursor was mechanically treated in isobutyl alcohol and agate was used as milling materials using planetary ball mill. The effect of ball milling process on the physico-chemical properties of catalysts was investigated by using several characterisation techniques.

Experimental

Preparation of Catalysts

The Mn-doped $VOHPO_4 \cdot \frac{1}{2}H_2O$ precursor was prepared by using organic method. Briefly, vanadium pentoxide, V_2O_5 (15.0 g from Fluka) and manganese chloride, $MnCl_2 \cdot 4H_2O$ (from BDH) with atomic ratio of Mn/V of 0.01 were suspended by rapid stirring into a mixture solution of benzyl alcohol (60 cm^3 from BDH) and isobutanol (90 cm^3 from BDH). After that, the mixtures were refluxed for 7 hrs at 393 K with continuous stirring. Then mixtures were cooled to room temperature and left stirring overnight. *Ortho*-phosphoric acid, H_3PO_4 (85% from Merck) was added slowly and stirred under refluxed for 3 hrs. The mixtures were cooled and the light blue solid was recovered by filtration, washed with water and then dried at 423 K for overnight. The ball mill experiment was carried out using planetary ball mill (model Pulverisette 7 from Fritsch) with agate bowl having 25 ml volume together with seven 12 mm diameter agate balls. About 4 g of the sample was ball milled for 60 min using isopropyl alcohol as solvent. The bowl spins around its own axis and around a second axis outside its centre at 800 revolutions per minute. The resulting milled and unmilled precursors were then undergone calcination in a flow of *n*-butane/air mixture (0.75% *n*-butane in air) for 75 hrs at 673 K to obtain active catalysts.

Catalysts Characterisation

X-ray diffraction (XRD) analyses were carried out using a Shimadzu diffractometer model XRD-6000 Diffractometer employing $Cu K_\alpha$ radiation generated by a Philips glass diffraction X-ray tube broad focus 2.7 kW type on the catalysts at ambient temperature.

Brunauer-Emmer-Teller (B.E.T.) surface area measurements were carried out using nitrogen adsorption-desorption at 77 K via ThermoFinnigan Sorptomatic 1990 instrument.

Scanning electron microscopy (SEM) was done using a JEOL JSM-6400 electron microscope.

Temperature-programmed reduction in hydrogen (H_2 -TPR), Temperature-programmed desorption of oxygen (O_2 -TPD) and ammonia (NH_3 -TPD) analyses were done by using a ThermoFinnigan TPDRO 1100 apparatus provided with thermal conductivity detector.

Results and Discussion

X-ray Diffraction (XRD)

The XRD patterns of Mn-doped precursor, as shown in Fig. 1, gave only characteristic reflection of vanadyl hydrogen phosphate hemihydrate, $VOHPO_4 \cdot \frac{1}{2}H_2O$ (JCPDS File No. 37-0269), with the main peaks appeared at $2\theta = 15.5, 19.6, 24.2, 27.0, 28.7, 30.4, 37.6$ and 49.2° . The XRD patterns of undoped precursor also show the characteristic reflection of $VOHPO_4 \cdot \frac{1}{2}H_2O$. Despite that milling process did not change precursor phase; however the peak intensity of the milled precursor is reduced. The crystallite size, which is calculated accordingly to Debye-Scherrer equation [12], shows that the size of the 60 min milled precursor is reduced to 39.2 nm, compared to the unmilled precursor (42.7 nm). Furthermore, the peaks along to (001) and (130) planes of the milled precursor are slightly shifted to $2\theta = 15.2$ and 30.1° , respectively, as compared to $2\theta = 15.6$ and 30.5° , respectively for the unmilled precursor. This observation suggested that a minor defect was occurred in the milled precursor because reflections of (020) and (204) planes in the $(VO)_2P_2O_7$ are related to (001) and (130) planes in the $VOHPO_4 \cdot \frac{1}{2}H_2O$ phase [1]. Table 1 shows that the increasing milling time led to increased full width at half maximum (FWHM) of the peaks along (001) and (130) planes. The increase in the relative peak intensities of $I_{(001)}/I_{(130)}$ of the milled precursor indicated that the exposure of (001) plane is increased which is contained the vanadyl group. Previous literatures [7,13] reported that the best effect in the improvement of selectivity can be reached by increase of the relative exposure of (001) plane at the $VOHPO_4 \cdot \frac{1}{2}H_2O$ surface which is known to be transformed into (020) plane of the $(VO)_2P_2O_7$.

Table 1
XRD data of precursors and catalysts

Time of milling, min	VOHPO ₄ ·1/2H ₂ O				(VO) ₂ P ₂ O ₇			
	I ₍₀₀₁₎ /I ₍₁₃₀₎	FWHM (001), deg	FWHM (130), deg	Crystallite size, nm	I ₍₀₂₀₎ /I ₍₂₀₄₎	FWHM (020), deg	FWHM (204), deg	Crystallite size, nm
0	91/100	0.21	0.17	42.7	97/100	0.41	0.35	21.6
60	100/92	0.22	0.20	39.2	89/100	1.00	0.73	9.7

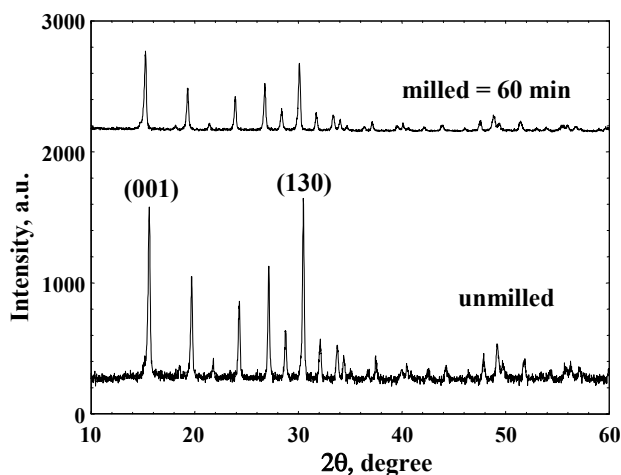


Fig. 1. XRD patterns of unground and milled precursors.

The (VO)₂P₂O₇ phase with the main peaks at $2\theta = 22.9, 28.5$ and 29.9° are only observed for all precursors after calcination in a flow of *n*-butane/air mixture for 75 hrs at 673 K (Fig. 2). These patterns show that the intensities of the peaks after milled are drastically decreased and FWHM values are increased. This indicates that particle size is reduced whereas the microstrain is increased [9].

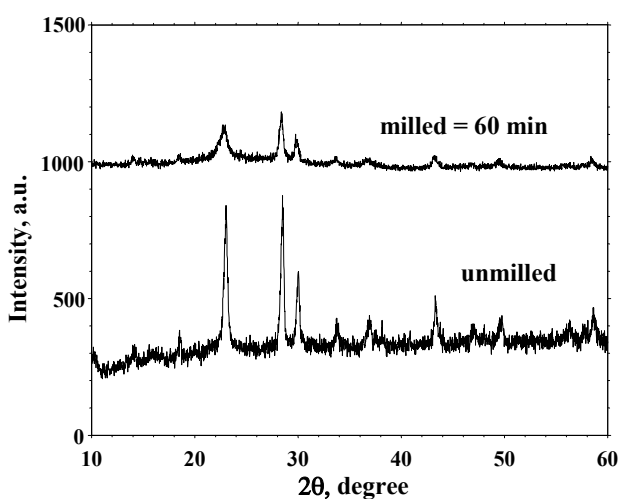


Fig. 2. XRD patterns of unground and milled catalysts.

B.E.T. Surface Area Measurements

The surface area of milled precursor ($9.8 \text{ m}^2\cdot\text{g}^{-1}$) is higher than unground precursor ($6.4 \text{ m}^2\cdot\text{g}^{-1}$), indicating ball milling process increased surface area as reported by previous literatures [7-9]. This result also in agreement with the results obtained from XRD and SEM, which indicated that crystallite size of the catalyst was reduced.

Scanning Electron Microscopy (SEM)

The surface morphologies of all unground and milled catalysts are shown in Figs. 3 and 4. The catalysts produced show secondary structure, consisting different sizes agglomeration of plate-like structure. Mechanochemical treatment caused lost their secondary structure and became more exposure with smaller plate-like structure.

Temperature-Programmed Desorption of Oxygen (O₂-TPD)

The O₂-TPD profiles for both unground and milled Mn-doped V-P-O catalysts shown in Fig. 5 were obtained by raising the temperature from ambient to 1173 K at $10 \text{ K}\cdot\text{min}^{-1}$ under helium stream (25 cm^3 .

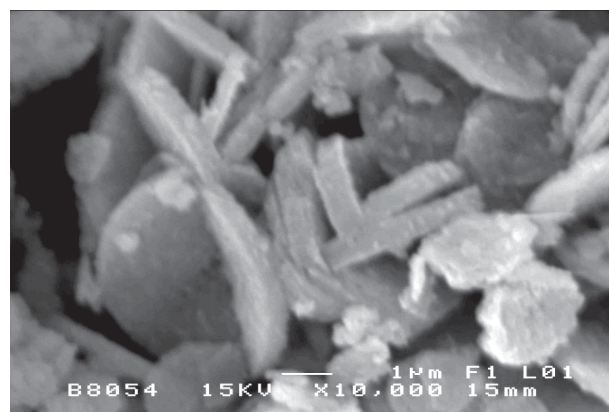


Fig. 3. SEM micrograph of unground catalyst.

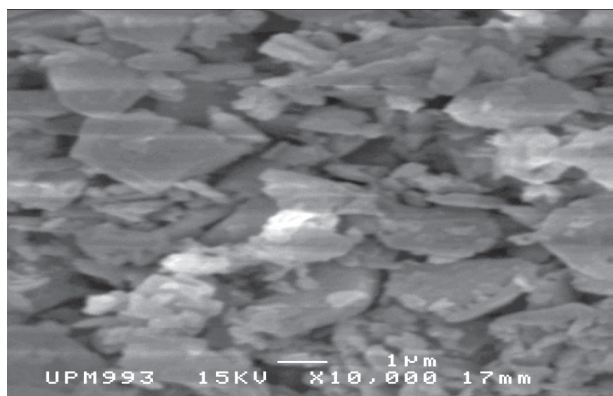


Fig. 4. SEM micrograph of 60 min milled catalyst.

min⁻¹, 1 bar) following the conductivity of the eluted gas. Before obtaining oxygen desorption spectra, the catalysts were pre-treated by heating them to 673 K in an oxygen flow (1 bar, 25 cm³·min⁻¹), holding them under that stream at 673 K for 1 h, before cooling them to ambient temperature. The unmilled and milled materials gave one peak maximum at 970 and 962 K, respectively. Table 2 shows that the total amount of the oxygen desorbed from unmilled material is 1.58·10²⁰ atom·g⁻¹. Interestingly, the total amount of the oxygen desorbed was doubled for milled material, *i.e.* 3.69·10²⁰ atom·g⁻¹. Previous report [14] had shown that these lattice oxygen are related to the selective oxidation of *n*-butane, but-1-ene and but-1,3-diene.

Temperature-Programmed Reduction in Hydrogen (H₂-TPR)

Further information on the behaviour of oxidizing species available from the catalysts were obtained by TPR analysis in H₂/Ar stream (5% H₂, 1 bar, 25 cm³·min⁻¹) of catalysts raising the temperature from ambient to 1273 K at 5 K·min⁻¹ in that stream. Figure 6 shows the H₂-TPR profiles of unmilled and milled catalysts. The unmilled catalyst gave three peaks maxima at 773, 892 and 1040 K, whereas three peaks maxima were observed at lower temperature

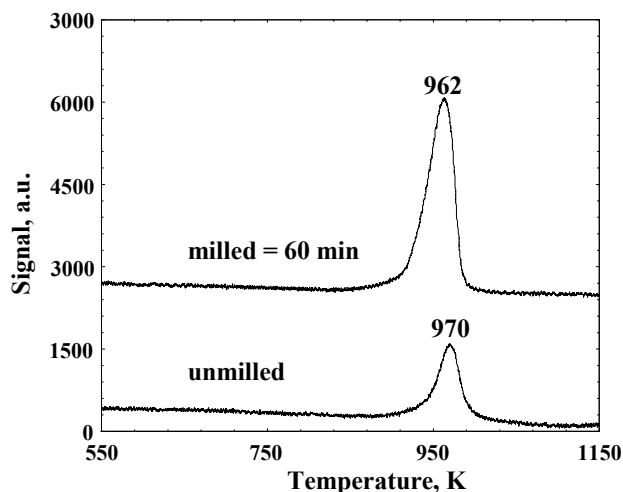


Fig. 5. O₂-TPD profiles of unmilled and milled catalysts.

zone (except the second peak) for 60 min milled catalyst, *i.e.* 751, 904 and 976 K. The total amount of oxygen removed being determined by quantification of the H₂ consumed obtained by integration area in the profile under the TPR peaks. Table 3 shows the values of reduction activation energies and the amount of oxygen removed. The total amount of oxygen removed for unmilled sample is 4.80·10²¹ atom·g⁻¹. Significantly, introduction of tribomechanical treatment for 60 min increased total amount of oxygen removed to 6.27·10²¹ atom·g⁻¹. The observation of (i) the peaks maxima shifted to lower temperature zone and (ii) increased of total amount of oxygen removed from the lattice concluded that milled catalysts which has higher mobility of lattice oxygen will give better catalytic performance for selective oxidation of *n*-butane to maleic anhydride.

Temperature-Programmed Desorption of Ammonia (NH₃-TPD)

The properties of the surface acidity of the catalysts were determined by using temperature-programmed desorption of ammonia. The NH₃-TPD profiles for unmilled and milled are shown in Fig. 7. After a pre-treatment at 473 K under nitrogen flow

Table 2

The values of reduction activation energies and total amount of oxygen removed of oxygen removed obtained by O₂-TPD

Sample	T _{max} , K	Desorption activation energy E _d , kJ·mol ⁻¹	Total amount of oxygen desorbed, mol·g ⁻¹	Total amount of oxygen desorbed, atom·g ⁻¹
unmilled	970	268	2.62·10 ⁻⁴	1.58·10 ²⁰
60 min	962	266	6.13·10 ⁻⁴	3.69·10 ²⁰

Table 3

The values of reduction activation energies and total amount of oxygen removed of oxygen removed obtained by H₂-TPR

Sample	Peak	T _{max} , K	Reduction activation energy E _r , kJ·mol ⁻¹	Total amount of oxygen removed, mol·g ⁻¹	Total amount of oxygen removed, atom·g ⁻¹
Unmilled	1	773	129	8.70·10 ⁻⁴	5.24·10 ²⁰
	2	892	149	1.09·10 ⁻³	6.57·10 ²⁰
	3	1040	174	6.01·10 ⁻³	3.62·10 ²¹
Total				7.97·10 ⁻³	4.80·10 ²¹
60 min	1	751	126	1.76·10 ⁻³	1.06·10 ²¹
	2	904	151	4.89·10 ⁻³	2.95·10 ²¹
	3	976	163	3.76·10 ⁻³	2.26·10 ²¹
Total				1.04·10 ⁻²	6.27·10 ²¹

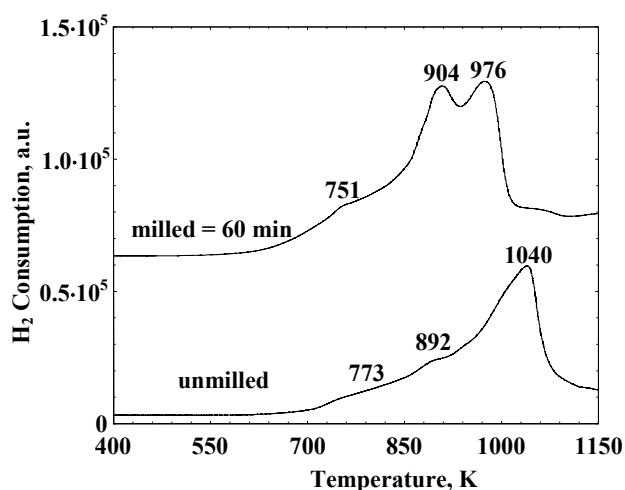


Fig. 6. H₂-TPR profiles of unground and milled catalysts.

for 30 min. The catalysts were cooled to room temperature under the same flow. After that, they were saturated with anhydrous ammonia at that temperature. The catalysts were then switched to He (20 cm³·min⁻¹, 1 bar) for 1 h at 423 K to desorb the physisorbed ammonia. Finally, the chemisorbed ammonia was desorbed by heating the catalysts from 423 to 873 K under that flow at 5 K·min⁻¹. The ammonia peak observed for unground sample reached a maximum at ~ 670 K and remained until it started dropping at ~ 810 K. However, milled material led to the desorption of the ammonia occurred at slightly lower onset temperature at ~ 551 K as well as maximum temperature, *i.e.* 615 K, indicating that surface acidity of the catalyst is increased for milled material. It is also supported by total amount of ammonia desorbed (1.44·10²¹ atom·g⁻¹) for 60 min is about 2 times higher than unground catalyst, *i.e.* 6.93·10²⁰ atom·g⁻¹.

The increment of the lewis acid site in the milled sample may due to the formation of higher amount of defect created by the tribomechanical treatment. Busca *et al.* [15] reported that this type of acid sites is strong Lewis sites coupled with a V=O double bond and responsible for the first step of activation of the *n*-butane. Haber *et al.* [16] reported that the selectivity to maleic anhydride is correlated with the connection of the acidic sites on the surface. They believed that the surface acidic sites affected selectivity by controlling adsorption of the reaction intermediate and maleic anhydride, which possesses acid properties. At low surface acidity, adsorption of adsorbed acid-like products is hindered, and they are overoxidized to CO_x. At high surface acidity, acidic reaction intermediate is desorbed from the surface before they are oxidized further into maleic anhydride.

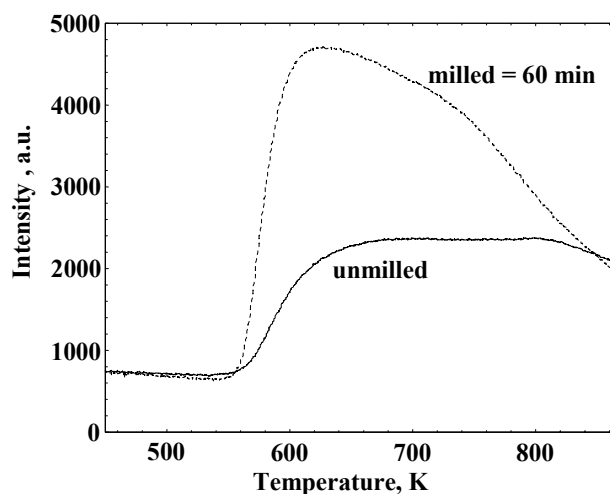


Fig. 7. NH₃-TPD profiles of unground and milled catalysts.

Conclusions

The phase of the $\text{VOHPO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ is still retained after ball milled for 60 min. Nevertheless, the process of ball milling has increased the values of FWHM of the materials, indicating that the crystallite size is decreased whereas the microstrain is increased. The concentration of (001) plane containing vanadyl group is increased after process of ball milling. A slightly increased of the surface area was observed for milled material. The process of milling significantly increased total amount of lattice oxygen being desorbed and removed from catalyst as well as shifted to the lower temperature zone. Besides, surface acidity of the catalysts is also increased after milling process.

Acknowledgements

Financial assistance from Malaysian Ministry of Science, Technology and Innovation is gratefully acknowledged.

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Received 15 May 2004.