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EFFECT OF MECHANOCHEMICAL TREATMENT ON $VOPO_4 \cdot 2H_2O$ TO PRODUCE VANADYL PYROPHOSPATE CATALYSTS

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ABSTRACT

Two vanadyl pyrophosphate catalysts were prepared via dihydrate route (VPD method) by applying mechanochemical treatment performed on $VOPO_4 \cdot 2H_2O$ in different duration of time, i.e. 30 and 60 min in ethanol medium. Both catalysts with the unmilled catalyst produced were characterized by x-ray diffraction (XRD), chemical analysis, scanning electron microscopy (SEM) and temperature programmed reduction (H_2-TPR). Catalytic evaluation for partial oxidation of n-butane to maleic anhydride (MA) was also being carried out using microreactor. XRD patterns of all the VPO catalysts showed the main peaks of pyrophosphate phase. TPR profiles showed that the mechanochemical treated VPO catalyst for 30 min (VPDM30) removed the active oxygen species at lower temperature. Furthermore, from the catalytic test results, the graph of the catalytic performance as a function of the duration of mechanochemical treatment demonstrates that VPDM30 is the most active catalyst. This suggested that the mechanochemical treatment of the $VOPO_4 \cdot 2H_2O$ for the synthesis of pyrophosphate catalyst (VPDM30) is highly potential to enhance the catalytic properties for n-butane oxidation towards maleic anhydride.

ABSTRAK

Dua mangkin vanadyl pyrophosphate telah disediakan melalui laluan dihydrate (Kaedah VPD) dengan menggunakan rawatan 'mechanochemical' yang dilakukan keatas VOPO4•2H¬2O dalam tempoh masa berbeza, iaitu 30 dan 60 min dalam bahantara etanol. Kedua-dua mangkin dengan pemangkin tidak dikisar yang dihasilkan telah dibuat pencirian unsur-unsur melalui kaedah belauan sinar-x (XRD), analisis kimia, kemikroskopan elektron imbasan (SEM) dan suhu pengurangan terancang (H2-TPR). Penilaian pemangkinan untuk pengoksidaan separa n butana untuk maleik anhidrida (MAK) juga telah dijalankan menggunakan microreactor. Pola-pola XRD semua mangkin VPO menunjukkan puncak utama itu pirofosfat fasa. Profil TPR menunjukkan yang pemangkin VPO diperlakukan mechanochemical untuk 30 min (VPDM30) membuang aktif spesis oksigen pada suhu lebih rendah. Tambahan pula, daripada bermangkin keputusan ujian, graf bermangkin prestasi seperti satu majlis tempoh mechanochemical rawatan menunjukkan yang VPDM30 adalah pemangkin paling aktif. Ini disarankan yang mechanochemical rawatan VOPO4•2H2O untuk sintesis pirofosfat pemangkin (VPDM30) adakah amat potensi untuk meningkatkan ciri-ciri pemangkin untuk n butana pengoksidaan ke maleik anhidrida.

Keywords: mechanochemical treatment; butane oxidation; vanadyl pyrophosphate

INTRODUCTION

Vanadium is a key element in the formulation of catalysts utilized in the production of anhydride via selective oxidation reaction in vapour phase with molecular oxygen[1]. Today, vanadium phosphorus oxide-based catalysts are still industrially employed for the selective oxidation of *n*-butane to maleic anhydride (MA)[2] whereby vanadium pentoxide were used as the starting material to synthesis such valuable catalysts.

In recent years, mechanochemical treatment has received great attention in the preparation of vanadium phosphate (VPO) catalysts[3]. Most efficient mechanochemical treatment of solid materials can be achieved in planetary ball mills. It has been shown that mechanochemical treatment of the $VOHPO_4 \cdot 0.5H_2O$ impairs a specific real structure that enhances the catalytic properties of the final catalysts, $(VO)_2P_2O_7$[4]. The enhanced catalytic performance is due to increase in surface area and the generation of fresh and reactive surfaces[5], enhanced exposure of the basal planes[6] and decreased particle size[4].

In this study, the physico-chemical properties of the vanadyl pyrophosphate catalysts synthesized *via* mechanochemical treatment with different duration of time using ethanol as the milling media were characterized by using x-ray diffraction (XRD), chemical analysis, scanning electron microscopy (SEM), temperature-programmed reduction (H_2-TPR). Catalytic oxidation of *n*-butane was also carried out to evaluate the catalytic behaviour.

EXPERIMENTAL

Preparation of mechanochemical treated VPO catalysts

12.0 g of V_2O_5, 57.4 ml of *ortho*–phosphoric acid and 288.0 ml of deionized water were reflux for 24 h at 393 K with constant stirring. The yellow slurry that was produced after the reflux process was filtered and washed with distilled water and acetone before drying at 373 K for 24 h. XRD analysis confirmed the yellow solid as $VOPO_4 \cdot 2H_2O$.

The mechanochemical treatment of vanadyl phosphate dihydrate, $VOPO_4 \cdot 2H_2O$ obtained was carried out by using planetary ball mill (model Pulverisette 4 from Fritsch) with an agate bowl having 250 cm^3 volume together with 50 agate balls (diameter = 10 mm). About 4.0 g of the $VOPO_4 \cdot 2H_2O$ and 80 cm^3 of ethanol as milling media were put together inside the bowl. The ball milling process was performed at the speed of 1400 revolutions per minute (rpm). Then, the samples were collected after 30 and 60 min. The resultant yellow solid ($VOPO_4 \cdot 2H_2O$ phase), was then recovered by using centrifuge technique and subsequently washed sparingly with distilled water and acetone and oven dried at 373 K for 24 h.

Mechanochemical treated $VOPO_4 \cdot 2H_2O$ obtained was then refluxed with isobutyl alcohol (1 g/20cm^3 from BDH) at 393 K for 21 h and the blue solid sample was centrifuged out from the solvent and dried in oven at 373 K for 24 h. The precursor obtained was calcined in reaction flow of 0.75 % *n*-butane/air mixture for 18 h at 733 K to generate the active catalyst denoted as VPDM30 and VPDM60.

Catalysts Characterization

The total surface area of the catalysts was measured by the Brunauer-Emmett-Teller (BET) method using nitrogen adsorption at 77 K. This was done by a Sorptomatic 1990 Series, Thermo Fischer-Scientific 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 numbers of vanadium in the sample bulk were determined by redox titration following the method of Niwa and Murakami[7].

X-ray diffraction (XRD) analysis was carried out by using a Shimadzu diffractometer model XRD 6000.

The electron microscopy techniques were used to obtain the information on the morphology and size of the samples by LEO 1455 Variable Pressure scanning electron microscopy (SEM). The morphology was studied at an accelerating voltage of 30 kV. The particles were attached on an aluminium stub by using double–sided tape. The preparation was covered by using a thin layer of gold coating by using BIO–RAD Sputter Coater. The SEM micrographs were recorded by using a digital camera at various magnifications.

H_2-TPR analysis was performed using ThermoFisher Scientific TPDRO 1100 apparatus equipped with a thermal conductivity detector (TCD). The experiment was done by following the thermal conductivity of the outlet stream with TCD when raising the temperature of the fresh catalysts was raised from ambient to 960 K at 10 K/min in a H_2/Ar stream.

The oxidation of *n*-butane was carried out at 673 K with GHSV = 2400 h^{-1} in a fixed-bed microreactor with a standard mass of catalyst (250 mg). *n*-Butane and air were fed to the reactor via calibrated mass flow controllers to give a feedstock composition of 1.0 % *n*-butane in air. The products were then fed via heated lines to an on-line gas chromatograph for analysis. The reactor comprised 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.

RESULTS AND DISCUSSIONS

X-ray diffraction (XRD)

The XRD patterns (Figure 1) of the mechanochemical treated in different duration of time and untreated vanadyl phosphate dihydrate obtained, $VOPO_4{\cdot}2H_2O$ are perfectly matched with the standard $VOPO_4{\cdot}2H_2O$ (JCPDS File No. 36-1472). The main characteristic peaks at $2\theta = 11.9°$, 23.9° and 28.8° are corresponding to (001), (002) and (200) planes, respectively.

The mechanochemical treatment process with 30 and 60 min duration of time that obtained vanadyl phosphate dihydrate, $VOPO_4{\cdot}2H_2O$, basically does not cause any changes, in terms of the basic matrix of the $VOPO_4{\cdot}2H_2O$ phase, which could be evidenced from the standard that being provided by the JCPDS. Hence, this further proves that no peaks of any other phases were detected indicating the high purity of the $VOPO_4{\cdot}2H_2O$ obtained that undergo for the mechanochemical treatment process compared to the untreated $VOPO_4{\cdot}2H_2O$.

Interestingly, the (001) diffraction plane for mechanochemical treated vanadyl phosphate dihydrate for 30 and 60 min, DM30 and DM60, shows more intense and narrower compared to the untreated vanadyl phosphate dehydrate which suggested that more crystallites form for the vanadyl phosphate dihydrate that undergo the mechanochemical treatment. This phenomenon occurred may be due to the mechanical shear forces in the mechanochemical treatment process that promotes the formation of smaller crystallite platelets that exposed to the environment which caused an increase in the intensity of the (001) diffraction plane. Hence, the degree of crystallinity of the (001) plane were markedly affected.

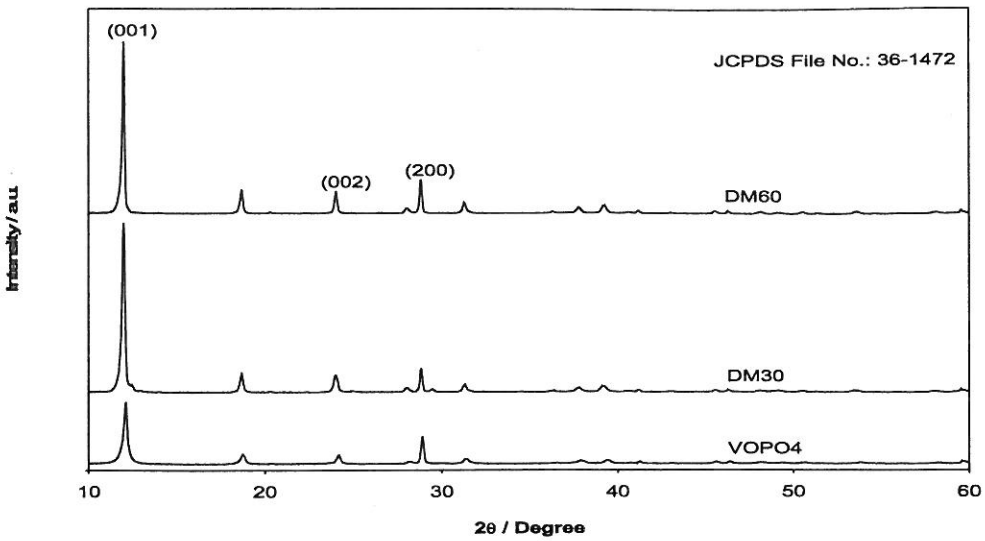


Figure 1: XRD patterns of mechanochemical treated and untreated vanadyl phosphate dihydrate

Figure 2 exhibited the XRD patterns of the VPO catalysts synthesized using vanadyl phosphate dihydrate which undergo mechanochemical treatment for 30 and 60 min, DM30 and DM60, compared to the bulk VPO catalyst that synthesized through the reduction of vanadyl phosphate dihydrate using conventional reflux method. All the VPO catalyst produced are very similar and shows characteristic of $(VO)_2P_2O_7$ phase with (020), (204) and (221) lines at 22.9°, 28.4° and 29.9°, respectively. No other VPO phase could be detected for all the catalysts synthesised indicating the catalysts produced mainly consist of active $(VO)_2P_2O_7$ as dominant phase which responsible for the partial oxidation of *n*-butane towards maleic anhydride[8].

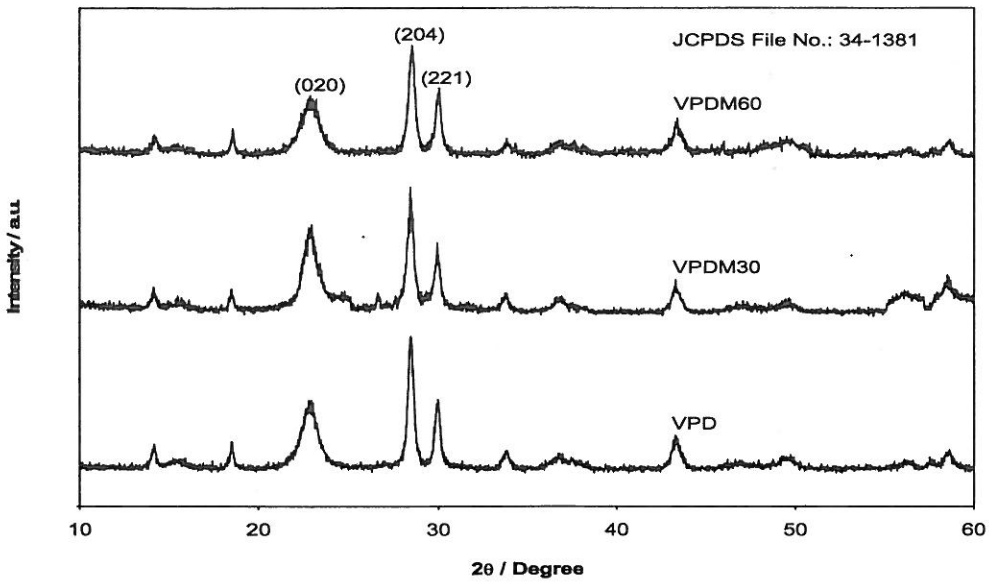
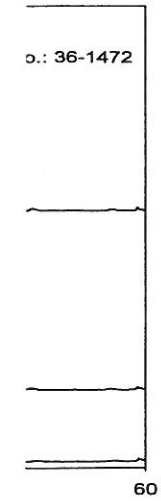


Figure 2: XRD patterns of mechanochemical treated and untreated VPO catalysts



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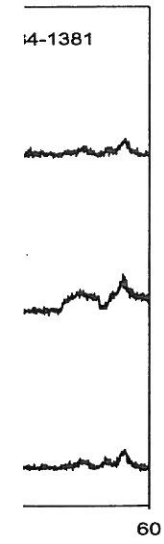

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BET Surface Area Measurements and Chemical Analysis

Table 1 exhibited the total surface area and chemical analysis results of mechanochemical treated and untreated catalysts. The VPO catalyst prepared via vanadyl phosphate dihydrate which undergo mechanochemical treatment, VPDM30 and VPDM60 gave similar surface area to the reference catalyst (VPD).

The P/V atomic ratios of the mechanochemical treated and untreated catalysts (Table 1) were slightly deviated from the nominal value of 1:1 ranging from the lowest value of 1.08 to the highest value of 1.09. However, these values are still fall within the intended optimal P/V atomic ratio range of 1.0-1.2 in producing a good $(VO)_2P_2O_7$ catalyst[9].

The average oxidation state of vanadium of 4.29, 4.24 and 4.06 given by VPD, VPDM30 and VPDM60, respectively. The mechanochemical treatment process at a prolonged time *i.e.* 60 min have drastically decreases the formation of V^{5+} phase ($VOPO_4$) from 29 % to 6 % for VPD and VPDM60, respectively. In other words, this mechanochemical treatment process promote the formation of more V^{4+} phase *i.e.* $(VO)_2P_2O_7$ that are active component for the maleic anhydride production.

Table 1: Specific BET surface area, chemical properties, average vanadium valence and percentages of V^{4+} and V^{5+} oxidation states present in mechanochemical treated and untreated catalysts

Catalysts	Specific BET Surface area (m^2/g)	Atomic ratio P/V	Oxidation of the Vanadium V^{4+} (%)	V^{5+} (%)	V_{av}
VPD	25.0	1.08	71	29	4.29
VPDM30	28.0	1.09	76	24	4.24
VPDM60	24.0	1.08	94	6	4.06

Scanning Electron Microscope (SEM)

The SEM micrographs (Figures 3-5) showed the mechanochemical treated and untreated catalysts consist of different sizes and secondary shape clusters that formed from the plate-like crystals. VPD catalyst produced (Figure 3) show the secondary structure, consisting of plate-like crystals, which are arranged into the characteristic of rosette-shape clusters. These rosette-shape clusters are made up of $(VO)_2P_2O_7$ aggregates that preferentially expose the (100) crystal plane[10], which had been proposed that the oxidation of $(VO)_2P_2O_7$ starts at the side of the (100) plane[11,12,13].

However, the VPO catalyst obtained via vanadyl phosphate dihydrate which undergo mechanochemical treatment for 30 min, VPDM30 (Figure 4), had lost its secondary rosette-shape clusters due to the mechanical shear force produced during the mechanochemical treatment process to form smaller crystal plates.

Unlike VPD catalyst, the crystal plates of VPDM60 catalyst obtained (Figure 5) via the reduction of mechanochemical treatment of $VOPO_4{\cdot}2H_2O$ for 60 min using conventional reflux method had arranged themselves to form sphere rosebud structure with uniform sizes and tend

to agglomerated with each other. These rosebud structures, which made up of $(VO)_2P_2O_7$ aggregates are preferentially exposing the (100) crystal plane as well[14].

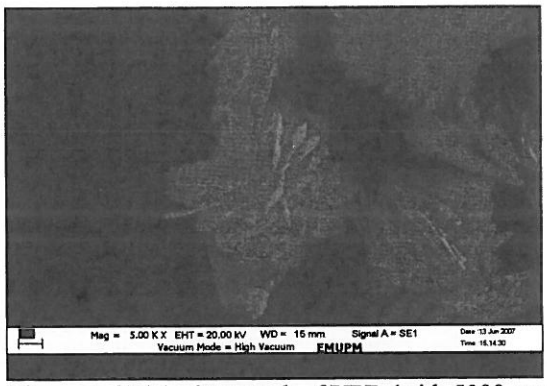

Figure 3: SEM micrograph of VPD (with 5000 × magnification)

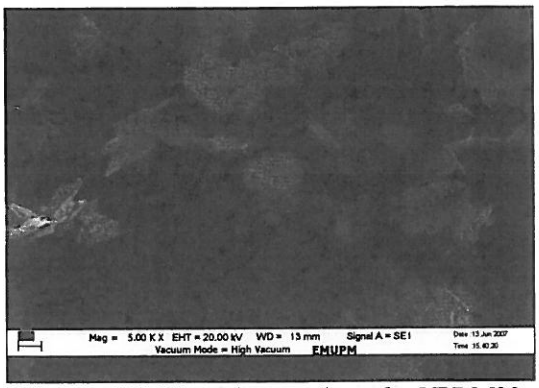

Figure 4:SEM micrograph of VPDM30 (with 5000× magnification)

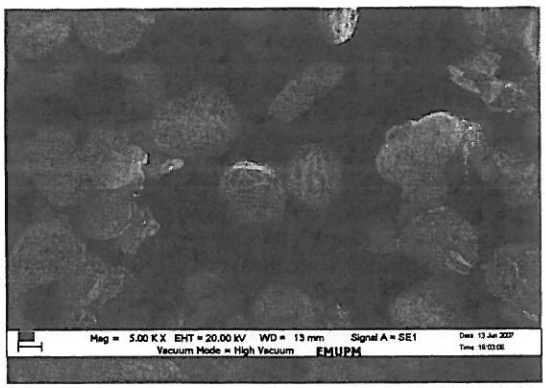

Figure 5: SEM micrograph of VPDM60 (with 5000× magnification)

of $(VO)_2P_2O_7$

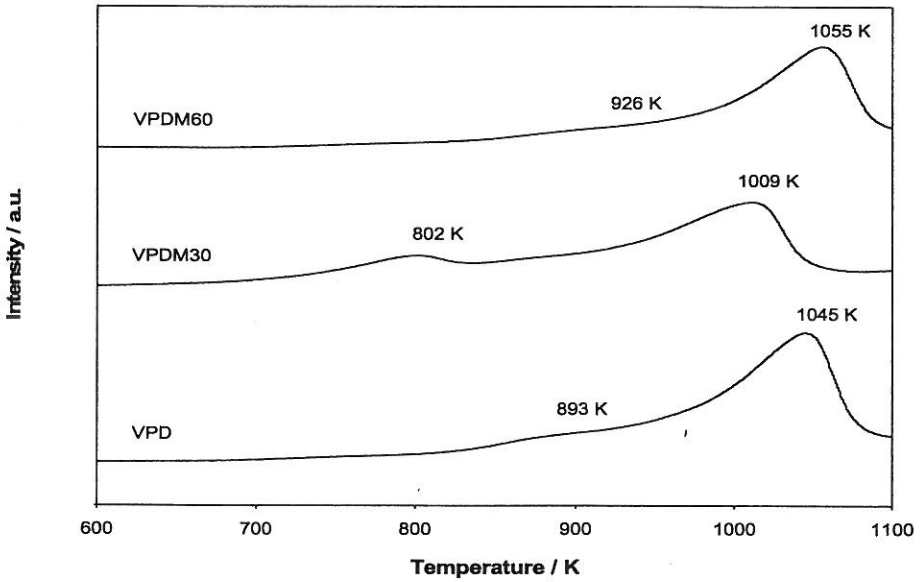

Figure 6: TPR profiles for VPD, VPDM30 and VPDM60 catalysts

Temperature Programmed Reduction (TPR in H_2/Ar)

H_2-TPR profiles and the total amount of oxygen removed from the catalysts synthesized were shown in Figure 6 and Table 2, respectively. VPD catalyst gave a characteristic of two reduction peaks occurred at 893 and 1045 K, which correspond to the reduction of V^{5+} and V^{4+} phases, respectively. The area of both peaks assigned to the removal of lattice oxygen species associated with the corresponding phases. The amount of oxygen removed from both peaks is 0.19×10^{21} and 1.35×10^{21} atom g^{-1}, respectively with an oxygen ratio removed from V^{5+}/V^{4+} of 0.14.

Interestingly, for VPDM30 catalyst, both reduction peak occurred at lower temperature compared to the VPD catalyst which is 802 and 1009 K, respectively. This proven that the lattice oxygen species in the V^{5+} and V^{4+} phases for VPDM30 catalyst are more reactive, mobile and can be removed more easily compared to the VPD catalyst.

Remarkably, VPDM30 catalyst also shows a drastically increased (47 %) of the oxygen species removed from V^{5+} phase with a decrease of 0.30×10^{21} atom g^{-1} on the amount of oxygen removed from V^{4+} phase compared to the VPD catalyst (Table 2). These give an oxygen species ratio from V^{5+}/V^{4+} of 0.26. A high amount of active oxygen released from V^{5+} phase (O^{2-}-V^{5+} pair) for VPDM30 catalyst may suggested that this catalyst to be more selective for maleic anhydride in partial oxidation of *n*-butane with a suitable oxygen species ratio from V^{5+}/V^{4+} of around 0.25 for best catalytic performance[15].

However, both reduction peaks fro VPDM60 were occurred at higher temperature compared to the VPD catalyst at 926 and 1055 K, respectively. This result shows that the lattice oxygen species both associated with V^{5+} and V^{4+} phases having stronger bonding and are more difficult to be removed. This can be further proven by the distinctive observations in the amount of oxygen removed from VPDM60 as summarized in Table 2. VPDM60 catalyst shows decrement (~11 %) of the oxygen species removed from V^{5+} phase with a decrease of 0.31×10^{21} atom g^{-1} on the amount of oxygen removed from V^{4+} phase compared to the VPD catalyst which give an oxygen species ratio from V^{5+}/V^{4+} of 0.16.

Table 2: Total amount of oxygen removed from VPD, VPDM30 and VPDM60 catalysts by reduction in H_2/Ar

Catalyst	T_{max} (K)	Oxygen Atom Removed ($\times 10^{-3}$ mol g^{-1})	Oxygen Atom Removed ($\times 10^{21}$ atoms g^{-1})	Ratio for oxygen removal of V^{5+}/V^{4+}
VPD				
1	893	0.31	0.19	0.14
2	1045	2.25	1.35	
Total oxygen atoms removed		2.56	1.54	
VPDM30				
1	802	0.47	0.28	0.26
2	1009	1.74	1.05	
Total oxygen atoms removed		2.21	1.33	
VPDM60				
1	926	0.29	0.17	0.16
2	1055	1.72	1.04	
Total oxygen atoms removed		2.01	1.21	

Catalytic Oxidation of n-Butane

As predicted based on the redox property of the catalysts, VPDM30 gave the highest activity with 43.0 % compared to only 25.0 % for untreated catalyst and 35.0 % for VPDM60 (Table 3). Higher reactivity of the oxygen species and surface area may contribute to the activity enhancement for VPDM30. Furthermore, the higher amount of oxygen species linked with V^{5+} phase also play a role to improve the activity of *n*-butane.

Table 3: The catalytic performance of mechanochemical treated and untreated VPO catalysts for oxidation of *n*-butane

Catalysts	*n*-Butane conversion (%)	Product selectivity (%)			MA yield (%)
		MA	CO	CO_2	
VPD	25.0	25.0	57.0	18.0	6.3
VPDM30	43.0	22.0	2.0	76.0	9.5
VPDM60	35.0	28.0	2.0	70.0	9.8

It should be noted that an appropriate amount of reactive O^- species released from V^{4+} phase (O^--V^{4+} pair) at lower temperature with a suitable oxygen species ratio from V^{5+}/V^{4+} of around 0.25 for best catalytic performance[15].

)M60 catalysts

:io for oxygen removal of V^{5+}/V^{4+}

0.14

0.26

0.16

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VPO catalysts

MA yield (%)

6.3
9.5
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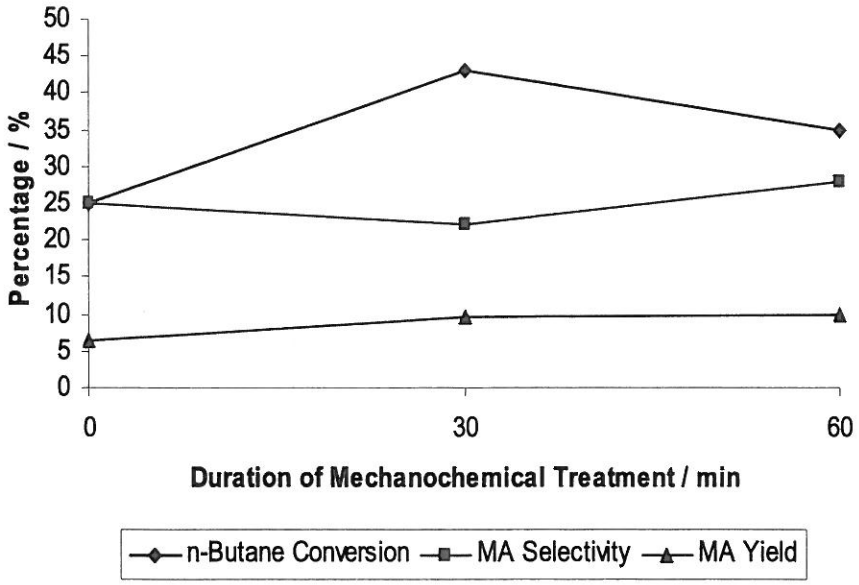

Figure 7: The catalytic performance of the synthesized VPO catalysts as a function of the duration of mechanochemical treatment

Moreover, the *n*-butane conversion rate of VPDM30 shown drastically increment of 18.0 % whereas VPO catalyst milled at its precursor stage ($VOHPO_4 \cdot 0.5H_2O$)[16] with the same condition drastically lowered by 20 %. This further suggested that an optimum duration for mechanochemical treatment for $VOPO_4 \cdot 2H_2O$ in ethanol is ~30 min whereas for $VOHPO_4 \cdot 0.5H_2O$ is ~60 min (Figure 7). These results suggested that different starting material will require specific or different duration for mechanochemical treatment in order to promote higher catalytic performance.

CONCLUSIONS

Mechanochemical treated vanadyl pyrophosphate catalyst, VPDM30 shows both reduction peaks occurred at lower temperature compared to the reference catalyst with a suitable oxygen species ratio from V^{5+}/V^{4+} of around 0.25. The lattice oxygen species in the V^{5+} and V^{4+} phases which are more reactive, mobile and can be removed easily shown to be the main contribution for VPDM30 to be the most active catalyst for *n*-butane oxidation. This further suggested that mechanochemical treatment of vanadyl dihydrate for 30 min in ethanol to produce vanadyl pyrophosphate catalyst is a potential method to improve the activity of the catalyst for partial oxidation of *n*-butane towards maleic anhydride.

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