



Effect of Different Calcination Duration on Physicochemical Properties of Vanadium Phosphate Catalysts

YUN HIN TAUFIQ-YAP^{*1,2}, HWEI VOON LEE¹, YIN CHANG WONG¹, KOK LEONG THEAM^{1,2} and WEN JIUNN TANG¹

¹Centre of Excellence for Catalysis Science and Technology, ²Department of Chemistry, Faculty of Science, Universiti Putra Malaysia. 43400 UPM Serdang, Selangor, Malaysia.

yap@science.upm.edu.my

Received 31 October 2011; Accepted 02 January 2012

Abstract: Vanadium phosphate catalysts have been prepared by calcining VOHPO₄·0.5H₂O which were prepared via two methods i.e. organic (VPO method) and dihydrate (VPD method) routes for different duration under anaerobic atmosphere. Increasing the calcinations duration led to a decrease in total surface area. It is also promote the formation of V⁵⁺ phase in the catalysts. Scanning electron microscopy clearly revealed that the morphologies of all catalysts composed of plate-like crystallites that were arranged into the characteristic of rosette cluster. However, by increasing the pretreatment duration in an inert environment, the rosette-shape of the clusters which normally obtained in reaction condition was collapsed. Prolong the duration of N₂ calcination also resulted in an increment in the amount of oxygen desorbed (from O₂-TPD) and removed (obtained from H₂-TPR).

Keywords: vanadium phosphate; oxygen; SEM; TPD; TPR.

Introduction

Vanadium phosphorus oxide has been extensively applied in the production of maleic anhydride from *n*-butane. All studies have focused on two specific phases, *i.e.* VOHPO₄·0.5H₂O and (VO)₂P₂O₇. The catalyst precursor VOHPO₄·0.5H₂O, which was subsequently transformed under reaction conditions to gave the vanadyl pyrophosphate, (VO)₂P₂O₇, which consider to be the active component of vanadium phosphate catalyst¹. The degree of crystallinity (morphology, presence of stacking faults, preferential exposure of crystalline planes, surface area) of the precursor phase has a considerable effect on the structural evolution during heating and the final properties of the (VO)₂P₂O₇. The transformation of the precursor to (VO)₂P₂O₇ involves two water-loss steps, the first associated with water of crystallization and the second with the transformation of hydrogen phosphate to pyrophosphate. The two transformations can occur simultaneously, depending on the nature of the precursor phase and the heat treatment². When oxygen is present in the atmosphere, there is also oxidation which leading to various possible V⁵⁺ phosphate phases (α_I, α_{II}, β, γ, δ) again depending on both the nature of the precursor phase and the conditions

of the heat treatment. Thus, there are a broad range of possibilities in terms of catalyst composition after the heat treatment step, with identification of some of the phases also being difficult³.

Our group has been investigated the effect of the different calcinations duration of *n*-butane/air pretreatment on the vanadium phosphate catalysts synthesized via organic method^{4,5}. In this paper, we would like to study the effect of different calcination duration on the vanadium phosphate catalysts prepared via VPO^{6,7} and VPD^{6,8,9} method. The precursors were calcined in an inert environment to produce catalysts which mainly consist of (VO)₂P₂O₇ phase.

Experimental

Preparation of Catalysts via VPO Method

The precursor of the promoted catalyst, VOHPO₄·0.5H₂O was prepared by reacting 8.0 g of V₂O₅, 48 ml of isobutyl alcohol and 32 ml of benzyl alcohol. The mixture was reflux for 7 h at 393 K with constant stirring. The solution was then cooled down and left stirring overnight. Then 10.2 ml of *o*-H₃PO₄ (85 %) was then added in to the solution to obtain the desired P:V atomic ratio. The mixture was further refluxed for 3 h at 393 K with constant stirring. The solid was recovered by centrifuge, washed sparingly with acetone, followed by water and dried in oven at 373 K for 24 h, and then identified by XRD as VOHPO₄·0.5H₂O. The precursors were calcined at the temperature 733 K for 6 hour, 24 hour and 48 hour in a reaction flow of nitrogen gas. The three catalysts obtained were denoted as VPO6, VPO24 and VPO48, respectively.

Preparation of Catalysts via VPD Method

The preparation of precursor involves a two-step procedure based on VOPO₄·2H₂O as an intermediate before obtaining the precursor, VOHPO₄·0.5H₂O. The VOPO₄·2H₂O was prepared by reacting 12.0 g of V₂O₅ with 57.4 ml of *o*-H₃PO₄ (85 %) in 288 ml water under reflux with continuous stirring for 24 h. The yellow solid was recovered by centrifuge, washed sparingly with acetone, followed by water and dried in oven at 373 K for 24 h, and then identified by XRD as VOPO₄·2H₂O. Then 4.0 g of VOPO₄·2H₂O was refluxed with 80 ml of isobutyl alcohol for 21 h. The solid was recovered by centrifuge, washed sparingly with acetone, followed by water and dried in oven at 373 K for 24 h, and then identified by XRD as VOHPO₄·0.5H₂O. The precursors were calcined at the temperature 673 K for 6, 24 and 75 h in a reaction flow of nitrogen gas. The three catalysts obtained were denoted as VPD6, VPD24 and VPD75, respectively.

Catalysts Characterization

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

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

The total surface area of the catalysts was measured by Brunauer–Emmett–Teller (BET) method by using nitrogen adsorption–desorption at 77 K. This was done by using a ThermoFinnigan Sorptomatic 1990 instrument.

The average oxidation states of vanadium in all the samples were determined by the method described by Niwa and Murakami¹⁰.

The bulk chemical composition was determined by using a sequential scanning inductively coupled plasma-atomic emission spectrometer (ICP-AES) Perkin Elmer Emission Spectrometer model Optima 2000 DV.

Temperature-programmed reduction in H₂/Ar (H₂-TPR) and Temperature-programmed desorption of oxygen (O₂-TPD) experiments were performed using a ThermoFinnigan TPD/R/O 1100 apparatus utilising a thermal conductivity detector (TCD).

Results and Discussion

X-ray diffraction (XRD)

The XRD patterns of catalysts are shown in Figure 1. These catalysts gave only the characteristic reflections of (VO)₂P₂O₇ with peaks observed at $2\theta = 22.9^\circ$, 28.5° and 30.0° which are corresponding to the reflection of (020), (024) and (221) planes, respectively. It is general believed that (VO)₂P₂O₇ is the active phase of VPO catalysts and the active crystal plane for selective oxidation of *n*-butane is the (020) plane¹¹. Interestingly, the catalysts synthesized via VPD method shows higher crystalline structure as the calcinations duration increased. VPD6 show the lowest crystalline structure, which indicated by the low intensity of the peak. This may due the insufficient calcination time for the precursor transform into (VO)₂P₂O₇ phase. Some researchers reported that the precursor first transforms into an amorphous phase^{12,13}, which can be further dehydrated to crystalline (VO)₂P₂O₇. The parameter which used to determine the degree of structural disorder of the VPO catalysts is the ratio of intensities of (020) and (204) reflections¹⁴. The different calcinations duration would affect the structural disorder of the VPD catalysts, because the ratio of intensities of the (020) and (204) reflections for VPD24 (0.83) and VPD75 (0.84) were lower than the VPD6 (1.38).

BET Surface Area Measurement and Chemical Analysis

Table 1 shows the experimental data on the P/V ratio, BET surface area and the percentage of V⁴⁺ and V⁵⁺ presence in the catalysts. Chemical analysis using ICP shows that the P/V ratio for all catalysts was in the optimal atomic ratio of P/V in the range of 1.0-1.2¹⁵. The BET surface area for VPO6, VPO24 and VPO48 catalysts are 11, 10 and 7 m²g⁻¹, respectively. Raising the calcination time decreased the surface area. These results were in contrast with our previous work where the precursors were calcined in the reactant mixture of *n*-butane in air⁴. The BET surface area for VPD6, VPD24 and VPD75 catalysts are 9, 6 and 4 m²g⁻¹ which is lower than the organic prepared catalyst. A slight reduction in the surface area with a longer calcination duration may probably due to the fact that less platelets per cluster catalyst are formed. These values are also lower than those reported earlier¹⁶⁻²⁰. The average vanadium oxidation number of the catalysts with longer calcination time was found higher compared to the catalysts with shorter calcination time. Both VPO6 and VPD6 have an average oxidation number of 4.00 and increased to 4.09, 4.08, 4.08 and 4.29 for VPO24, VPO48, VPD24 and VPD75, respectively.

Scanning Electron Microscopy (SEM)

Figure 3 show the surface morphologies of the catalysts with different calcination time. The structure of all catalysts were consist of plate like platelets which are arranged into the rosette-shape clusters^{4,21,22}. However, the amounts of these characteristic rosette-shape agglomerates are different in all catalysts. VPO6 catalyst possesses more uniform rosette-type clusters than VPO24 and VPO48 catalysts. This should be the reason for the higher surface area of VPO6 compared to VPO24 and VPO48. There appeared to be a consistency whereby the amount of these rosette-type agglomerates decreased with increasing the calcinations time for the catalysts prepared by using VPO method.

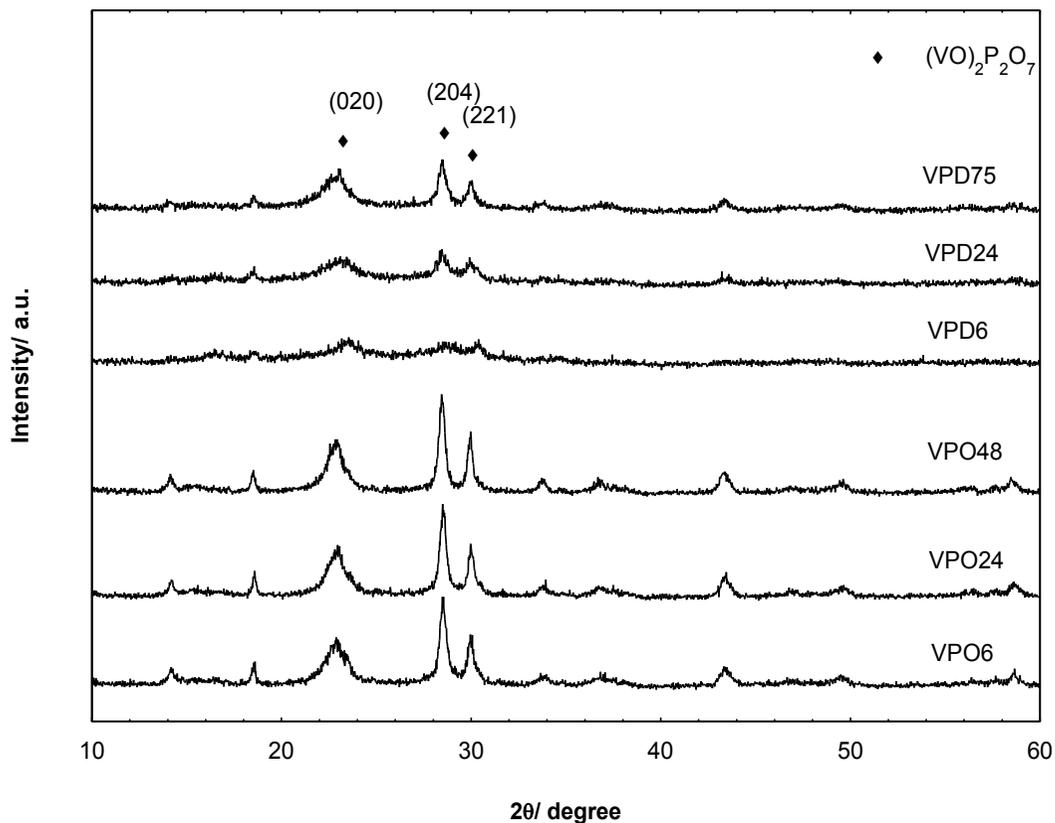


Figure 1. X-ray diffraction patterns of catalysts.

Comparison of the VPD6, VPD24 and VPD75 SEM images revealed that the catalyst which had been calcined for the longest duration, *i.e.* VPD75, appeared to have less prominent rosette-shape clusters and the structure started collapse as compared to its less calcined counterparts. This is in agreement with the results obtained from BET surface area measurements, *i.e.* the surface area of VPD6 is higher than the samples with longer calcination time.

Temperature-programmed Desorption of O₂ (O₂-TPD)

Figure 3 shows the TPD profiles of the catalysts. There was no desorption peak appeared at any temperature for VPO48 catalyst as compared to other catalysts. This result suggested that the oxygen species of VPO48 is likely to be less labile and reactive among the catalysts. VPO6 and VPO24 catalysts gave only one peak maximum at 963 K and 811 K, respectively. As shown in Table 2, the amount of oxygen desorbed from VPO6 is 3.55×10^{19} atom g⁻¹. Interestingly, VPO24 gave higher amount of oxygen desorbed from the lattice *i.e.* 19.39×10^{19} atom g⁻¹. The significant higher amount of oxygen desorbed from VPO24 may possibly be due to the lower desorption peak temperature which contributed to a lower desorption activation energy required for removal of more oxygen atoms from the lattice.

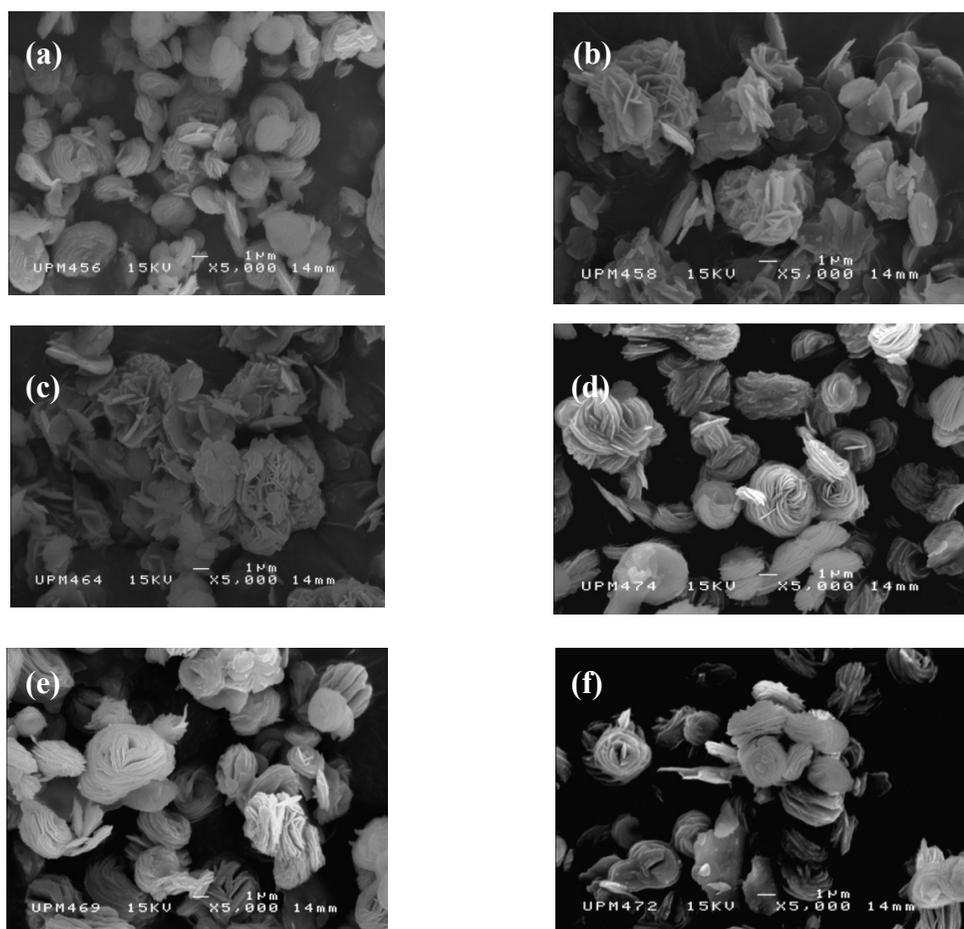


Figure 2. SEM micrographs for (a) VPO6, (b) VPO24, (c) VPO48, (d) VPD6, (e) VPD24 and (f) VPD75.

The amount of oxygen desorbed for VPD6, VPD24 and VPD75 are 16.86×10^{19} , 13.25×10^{19} and 31.92×10^{19} atom g^{-1} , respectively. VPD75 possess the highest amount of oxygen desorbed suggested that this catalyst may possibly favour a higher selectivity.

Table 1. Surface area, bulk composition, average oxidation states and percentage of V^{4+} and V^{5+} oxidation states present in catalysts.

Catalysts	Surface area (m^2g^{-1})	P/V Atomic Ratio	Oxidation States of Vanadium		
			V^{4+} (%)	V^{5+} (%)	Average
VPO6	11	1.1	100	0	4.00
VPO24	10	1.1	91	9	4.09
VPO48	7	1.0	92	8	4.08
VPD6	9	1.1	100	0	4.00
VPD24	6	1.0	92	8	4.08
VPD75	4	1.0	71	29	4.29

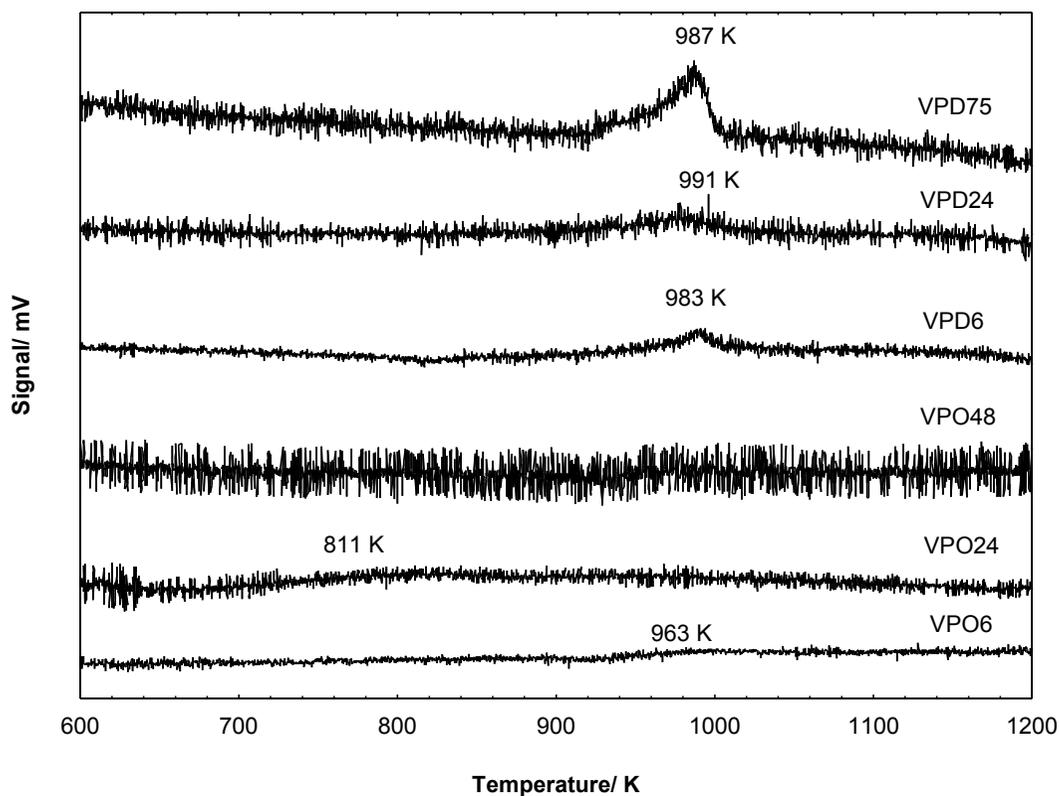


Figure 3. Temperature programmed desorption of O₂ from catalysts.

Table 2. O₂-TPD data obtained from catalysts.

Catalysts	T _{max} (K)	Desorption Activation Energy, E _d /kJ mol ⁻¹	Oxygen atoms removed/ × 10 ⁻⁴ mol g ⁻¹	Oxygen atoms removed/ × 10 ¹⁹ atom g ⁻¹
VPO6	963	265.9	0.59	3.55
VPO24	811	224.0	3.22	19.39
VPO48	-	-	-	-
VPD6	983	271.5	2.80	16.86
VPD24	991	273.7	2.20	13.25
VPD75	987	272.6	5.30	31.92

Temperature-programmed reduction (TPR)

The amount and nature of the oxygen species of all the catalysts were investigated by temperature-programmed reduction in H₂/Ar stream (5% H₂ in Ar, 1 bar, 25 cm³ min⁻¹), using a fresh catalyst and raising the temperature from ambient to 1150 K at 10 K min⁻¹. Figure 4 shows the profiles of H₂-TPR for the catalysts. The total oxygen removed, the derived reduction activation energies and the ratio for oxygen removal from V⁵⁺/V⁴⁺ by reduction in H₂/Ar is summarized in Table 3. One reduction peak of hydrogen consumption was observed for VPO6 and VPD6 at 1058 K and 983 K, respectively, which correspond to the reduction of V⁴⁺ phases²³. The results were in agreement with the redox titration results which show only the V⁴⁺ phase was present in the VPO6 and VPD6 catalysts. By increasing the calcination duration, the catalysts gave two reduction peaks and the additional peak is assigned to the removal of lattice oxygen from the V⁵⁺ phase²³. The TPR profiles show the first reduction peak for VPO24 VPO48, VPD24 and VPD75 which are less prominent compared to the second reduction peak. This is also in agreement with the redox titration where lower percentages of V⁵⁺ phase were obtained for these catalysts. Small amount of V⁵⁺ phases in the major well crystalline pyrophosphate phase will enhance the catalytic performance of a vanadium phosphate catalyst²⁴.

The amount of oxygen removed by H₂ is 1.3×10^{21} atom g⁻¹ for VPO6. Interestingly, the total oxygen removed significantly increased to 1.85×10^{21} atom g⁻¹ for VPO24 due to the higher oxygen species released associated with V⁴⁺ and V⁵⁺. However, further calcine to 48 h reduced the total amount of oxygen removed to 1.63×10^{21} atom g⁻¹. For the catalysts synthesized by using VPO method, we suggested that 24 h of calcination time in an inert environment is the optimum duration to produce a catalyst with better catalytic performance as the VPO24 possesses more labile and highest amount of active V⁴⁺-O⁻ pair for *n*-butane activation^{24,25} and V⁵⁺-O²⁻ pair for promoting the selectivity to maleic anhydride²⁵⁻²⁶.

Table 3. Total number of oxygen atoms removed from catalysts by reduction in H₂/Ar.

Catalysts	Peak	T _{max} (K)	Oxygen atoms removed/ $\times 10^{-3}$ mol g ⁻¹	Oxygen atoms removed/ $\times 10^{21}$ atom g ⁻¹
VPO6	1	1058	2.15	1.3
Total Oxygen atoms removed			2.15	1.3
VPO24	1	786	0.47	0.29
	2	1064	2.59	1.56
Total Oxygen atoms removed			3.06	1.85
VPO48	1	801	0.20	0.12
	2	1067	2.51	1.51
Total Oxygen atoms removed			2.71	1.63
VPD6	1	983	2.29	1.38
Total Oxygen atoms removed			2.29	1.38
VPD24	1	908	1.14	0.69
	2	1038	1.63	0.98
Total Oxygen atoms removed			2.77	1.67
VPD75	1	795	0.89	0.54
	2	1069	2.29	1.38
Total Oxygen atoms removed			3.18	1.92

The amount of oxygen removed from VPD6 is 1.38×10^{21} atom g^{-1} . By increasing the duration of calcination of precursor to 24 h, VPD24 catalyst gave a characteristic of two reduction peaks which occurred at 908 and 1038 K, respectively. VPD75 catalyst gave similar characteristic of two peaks with VPD24 catalyst. The first peak occurred at 795 K and the later peak occurred at 1069 K. The first reduction peak of VPD75 shifted towards lower temperature at 795 K compared to VPD24 catalyst. The results indicated that VPD75 catalyst possesses higher mobility of O^{2-} species at low temperature. There are appeared to be a consistency whereby the total amount of oxygen release from the catalysts increased with increasing calcinations time, *i.e.* 1.67×10^{21} atom g^{-1} and 1.92×10^{21} atom g^{-1} for VPD24 and VPD75, respectively. A higher amount of oxygen removed from the VPD75 suggested that this catalyst will give higher activity and selectivity for *n*-butane oxidation compared with the less calcined samples.

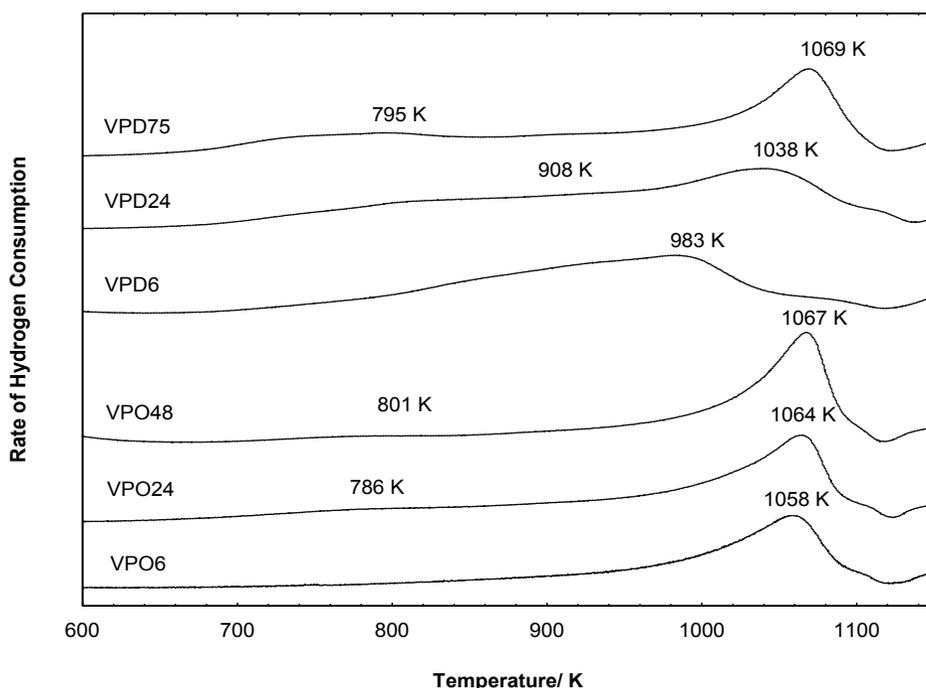


Figure 4. H_2 -TPR profiles of catalysts.

Conclusions

1. Increasing the calcination duration of vanadium phosphate catalysts prepared via VPO and VPD method in N_2 environment induced the formation of V^{5+} phase and lowering the surface area of the catalysts. The morphology of all the catalysts is shown to be in rosette shape. However, the shape was getting cracked and lost as the calcination time prolonged.
2. The consumption of H_2 in TPR shows that more lattice oxygen can be removed for the 24 h calcined catalyst which synthesized via VPO method. Besides, the catalysts prepared by using VPD method shows that more amount of oxygen can be removed by H_2 after the longer period N_2 pretreatment and it is suggested that the longer duration of N_2 pretreatment will give a more active and selective catalyst.

Acknowledgement

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

References

1. Hutchings G J *J. Mater. Chem.* 2004, **14**, 3385.
2. Cavani F, Centi G, Trifirò F and Poli G *J. Therm. Anal.* 1985, **30**, 1241.
3. Centi G, Cavani F and Trifirò F, *Selective Oxidation by Heterogeneous Catalysis*. Kluwer Academic/Plenum Publishers: New York, 2001, 143.
4. Taufiq-Yap Y H, Looi M H, Waugh K C and Hussein M Z *Catal. Lett.* 2001, **74**, 99.
5. Waugh K C and Taufiq-Yap Y H *Catal. Today* 2003, **81**, 215.
6. Horowitz H S, Blackstone C M, Sleight A W and Teufer G *Appl. Catal.* 1988, **38**, 193.
7. Johnson J W, Johnston D C, Jacobson A J and Brody J F *J. Chem. Soc.* 1984, **106**, 8123.
8. Hutchings G J, Olier R, Sananes M T and Volta J C *Stud. Surf. Sci. Catal.* 1994, **82**, 213.
9. Taufiq-Yap Y H, Goh C K, Waugh K C and Kamiya Y *React. Kinet. Catal. L.* 2007, **84**, 271.
10. Niwa M and Murakami Y *J. Catal.* 1982, **76**, 9.
11. Shen S, Zhou J, Zhang F, Zhou L and Li R *Catal. Today* 2002, **74**, 37.
12. Hodnett B K and Delmon B *Appl. Catal.* 1984, **9**, 203.
13. Cheng W-H and Wang W *Appl. Catal. A-Gen.* 1997, **156**, 57.
14. Poli G, Resta I, Ruggeri O and Trifirò F *Appl. Catal.* 1981, **1**, 395.
15. Centi G, Cavani F and Trifirò F, *Selective Oxidation by Heterogeneous Catalysis*. Kluwer Academic / Plenum Publishers: New York, 2001, 156.
16. Griesel L, Bartley J K, Wells Richard P K and Hutchings G J *J. Mol. Catal. A- Chem.* 2004, **220**, 113.
17. Taufiq-Yap Y H, Tan K P, Waugh K C, Hussein M Z, Ramli I and Abdul Rahman M B *Catal. Lett.* 2003, **89**, 87.
18. Taufiq-Yap Y H, Kamiya Y and Tan K P *J. Nat. Gas Chem.* 2006, **15**, 297.
19. Taufiq-Yap Y H, Goh C K and Kamiya Y *React. Kinet. Catal. L.* 2007, **92**, 275.
20. Taufiq-Yap Y H and Abdul Ghani A A *Chinese J. Catal.* 2007, **28**, 1037.
21. Kiely C J, Burrows A, Sajip S, Hutchings G J, Sananes M T, Tuel A and Volta J C *J. Catal.* 1996, **162**, 31.
22. Hutchings G J *J. Mater. Chem.* 2004, **14**, 3385.
23. Pierini B T and Lombardo E A *Mater. Chem. Phys.* 2005, **92**, 197.
24. Taufiq-Yap Y H *J. Nat. Gas Chem.* 2006, **15**, 144.
25. Taufiq-Yap Y H, Goh C K, Hutchings G J, Dummer N and Bartley J K *J. Mol. Catal. A-Chem.* 2006, **260**, 24.
26. Sananes M T, Tuel A, Hutchings G J and Volta J C *J. Catal.* 1997, **166**, 388.

