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OPTIMIZATION OF THE SURFACE AREA OF V_2O_5 NANOCRYSTALS THROUGH NUMBER OF WASHING

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ABSTRACT

In this study, vanadium pentoxide, V_2O_5 were synthesized by precipitating ammonium vanadate with ammonium hydroxide in increasing pH method. The solid precipitates obtained were then subjected to different number of washing and its effect on the microstructural properties of V_2O_5 was studied. TGA result suggested that 500 °C was the best temperature to transform the precursor into the desired products. This has been confirmed by the XRD result of calcined samples which showed diffractograms matched perfectly with V_2O_5 phase. The V_2O_5 particles sizes were in nanometre range between 24 – 62 nm. SEM morphology revealed that the particles showed rectangular shape before and after calcined with holes and cracks surfaces compared to a rather smooth surface in the precursor. This suggested that upon heat treatment, all the impurities have been successfully eliminated and in doing that, they left holes and cracks. Specific surface area, S_{BET} of the unwashed sample gave highest value ($6.1 m^2 g^{-1}$) compared to the others samples. The low S_{BET} value for the latter sample was probably due to peptization process occurred during the washing step.

INTRODUCTION

The principal oxides of vanadium occur as single valence oxides in the oxidation states from V^{2+} to V^{5+}, which is the form of VO, V_2O_3, VO_2 and V_2O_5 [1, 2]. The most important oxidation states of vanadium oxides in aqueous solution are V^{5+} and V^{4+}. Vanadium forms several acidic oxides with the dark green trioxide (V_2O_3) and the orange vanadium pentoxide (V_2O_5) represent the most important materials [3, 4]. Vanadium oxide is an excellent catalyst used in the manufacture of important chemicals including sulphuric acid and phthalic acid. In the production of sulphuric acid, V_2O_5 act as catalyst in the oxidation of SO_2 to SO_3. Supported vanadium oxide catalyst also represented as industrially important active catalyst. For example, the $V_2O_5/WO_3/TiO_2$ catalysts were employed in the selective catalytic reduction of nitrogen oxides [5]. In this study, works have been carried out to study the washing effect on the vanadium oxide catalyst. It is believe that the washing process will affect the catalyst physicochemical properties including its purity, crystallinity and textural properties.

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EXPERIMENTAL DETAILS

Samples preparation

Vanadium oxide was prepared by using the precipitation method. Ammonium metavanadate, NH_4VO_3 (BDH) was used as a starting material by dissolving it completely in nitric acid, HNO_3 (Prochem). The solution was titrated with 5.0 M ammonium hydroxide, NH_4OH (Prochem) at constant stirring and dropping rate. The pH value was measured for every additional of 10 ml of NH_4OH. Titration was stopped when pH of the solution became constant at pH 7.7. The precipitates were then aged for 1 day before divided equally into 5 portions where each container was labelled as Portion 1, 2, 3, 4 and 5. The precipitates were then filtered using a Buchner apparatus. Portion 1 was directly filtered without undergone washing. This sample was a control on comparing the effect of washing. Whereas Portion 2 was washed with 50 ml of deionised water, followed by Portion 3, which was washed two times using 50 ml of deionised water. Portion 4 and Portion 5 were washed three and four times, respectively using 50 ml of deionised water each time. The white precipitates were later dried in air before they were activated in air at 773 K for 5 h. Calcined samples were then denoted as VO1, VO2, VO3, VO4 and VO5.

Samples characterization

The powder X-ray diffraction patterns were recorded by using a Shimadzu Diffractometer Model XRD 6000 with scanning rate at 2.0000° min^{-1}. The estimate of crystallite sizes were calculated by using Debye-Scherer formula from the peaks obtained. The surface morphology and specific surface area measurement, S_{BET} of the samples were observed with a JEOL JSM-6400 electron microscope and Thermo Finnigan Sorptomatic 1990 instrument respectively.

RESULTS AND DISCUSSION

Titration curve

Figure 1 displays titration curve of vanadium solution precipitated with 5.0 M NH_4OH. Initially the clear vanadate solution was in yellow colour as this is the characteristic of vanadium in the form of VO_2^+. The beginning addition of NH_4OH to vanadium solution resulted in a downward sloping curve, as the vanadate solution is extremely acidic. Visible precipitation begin roughly after 480 ml addition of precipitating agent and from that point, an addition of more NH_4OH resulted in formation of more red-brown gelatinous particles. As the pH of solution increased to 0.90, a dark brown precipitate was formed which indicates the presence of $V_4O_9^{2-}$ and VO_4^{4-} at higher pH value. The titration reached the equivalence point at pH 2.56 and a steep slope was observed from pH 0.90-5.26. As the precipitation proceeds, pH of the solution increased continuously. Dark green precipitate appeared after addition of 860 ml NH_4OH and this signified the existence of V^{3+}. pH value of solution became constant at pH ~ 7.0. At this stage, the

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precipitate obtained was in white colour and no colour changes were observed upon addition of more precipitating agent. Growth process was believed prevails at this stage.

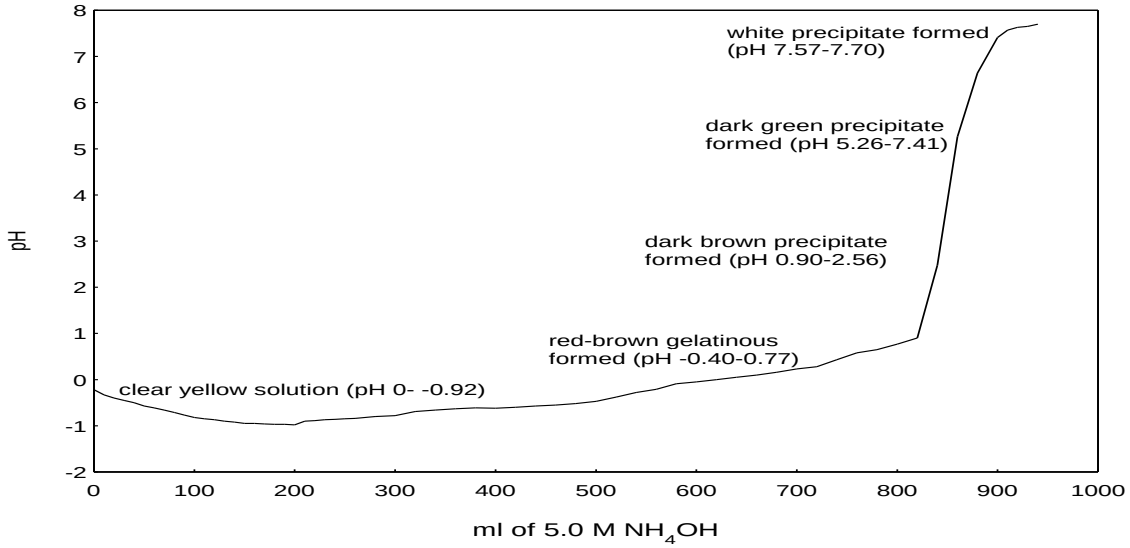

Figure 1: pH-volume response of precipitation process.

X-ray Diffraction (XRD)

According to the XRD patterns (Fig 2), the freshly calcined samples were composed of pure V_2O_5 (JCPDS File No. 41-1426) which main peaks appeared at 2θ = 20.28 º, 26.23 º and 31.08 º. All of the calcined samples are well crystalline as shown by the highly intense and sharp peaks. The XRD diffratograms on calcined samples revealed no clear effect of washing process on the formation of vanadium pentoxide. All of the samples showed similar diffractograms. Further analysis was carried out on the XRD diffractograms of the calcined samples. An estimation of the crystallite size based on X-ray peaks broadening can be calculated using Debye-Scherrer equation as below:

$$Crystallite\ size,\ t = \frac{0.9\lambda}{\beta_{hkl}\cos\theta_{hkl}}$$

where t is the crystallite size for (hkl) phase, λ is the X-ray wavelength of radiation for Cu Kα, β_{hkl} is the full-width at half maximum (FWHM) at (hkl) peak in the radian and θ_{hkl} is the diffraction angle for (hkl) phase. The crystallite size, t are summarized in Table 1. The calculated crystallite sizes are in the range of 24-62 nm. The up and down of the crystallite sizes for VO1 to VO5 are possibility due to the peptization process. Peptization is essentially a breakdown or a reconstruction process that allow the rearrangements to take place even at a smallest scale. The specific surface area measurement, S_{BET} were carried out on the calcined samples are presented in column 2 of Table 1. From the data, the unwashed sample, VO6 gave the highest $S_{BET,}$ 6.14 m^2g^{-1} compared to the other samples. This value is higher than what have been reported by I.E. Wachs *et. al*. [6] where the S_{BET} for V_2O_5 is 3.50 m^2g^{-1}. Peptization that occurs

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during washing process allowed the superfine particles come together to form bigger ones and resulted in smaller S_{BET} value. The obtained result is also in agreement with the XRD result that been discussed earlier where the calculated sample that undergone three times washing process displayed the largest crystallite size. Therefore, it will give smaller surface area.

Table 1: Variation of surface area and crystallite size calculation based on XRD data

Samples	S_{BET} ($m^2 g^{-1}$)	$FWHM_{301}$[a]	t_{301} (nm)	$FWHM_{001}$[b]	t_{001} (nm)	$FWHM_{200}$[c]	t_{200} (nm)
VO1	6.14	0.1438	62.2	0.1907	42.3	0.2191	25.1
VO2	5.00	0.1587	58.2	0.2101	41.8	0.2278	24.2
VO3	2.91	0.1477	62.6	0.1809	50.0	0.1924	29.6
VO4	4.89	0.1484	62.3	0.2029	42.4	0.2088	25.1
VO5	3.93	0.1533	56.6	0.1935	44.4	0.1974	31.2

[a] FWHM for (301) crystal plane of V_2O_5 [b] FWHM for (001) crystal plane of V_2O_5
[c] FWHM for (200) crystal plane of V_2O_5

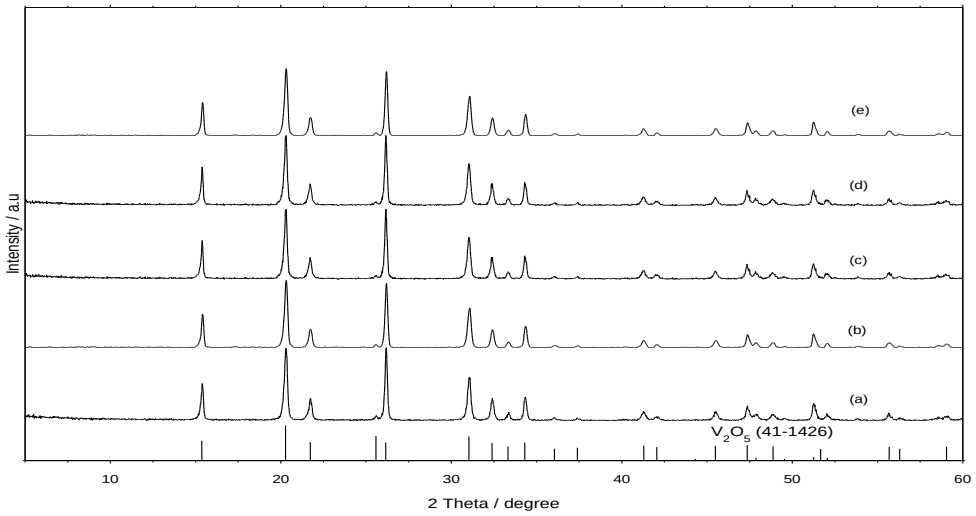

Figure 2: XRD diffractograms of V_2O_5 catalysts: (a) VO1, (b) VO2, (c) VO3, (d) VO4 and (e) VO5.

Scanning Electron Microscopy (SEM)
The SEM images recorded on different number of washing samples are shown in Figures 3. Through SEM micrographs, it indicated that washing process had no effect on the morphologies of the calcined samples as all of them showed alike images since the particles retained their rectangular shape. Cracks and holes that been observed on the calcined samples are due to the space created when impurities were removed during heating process.

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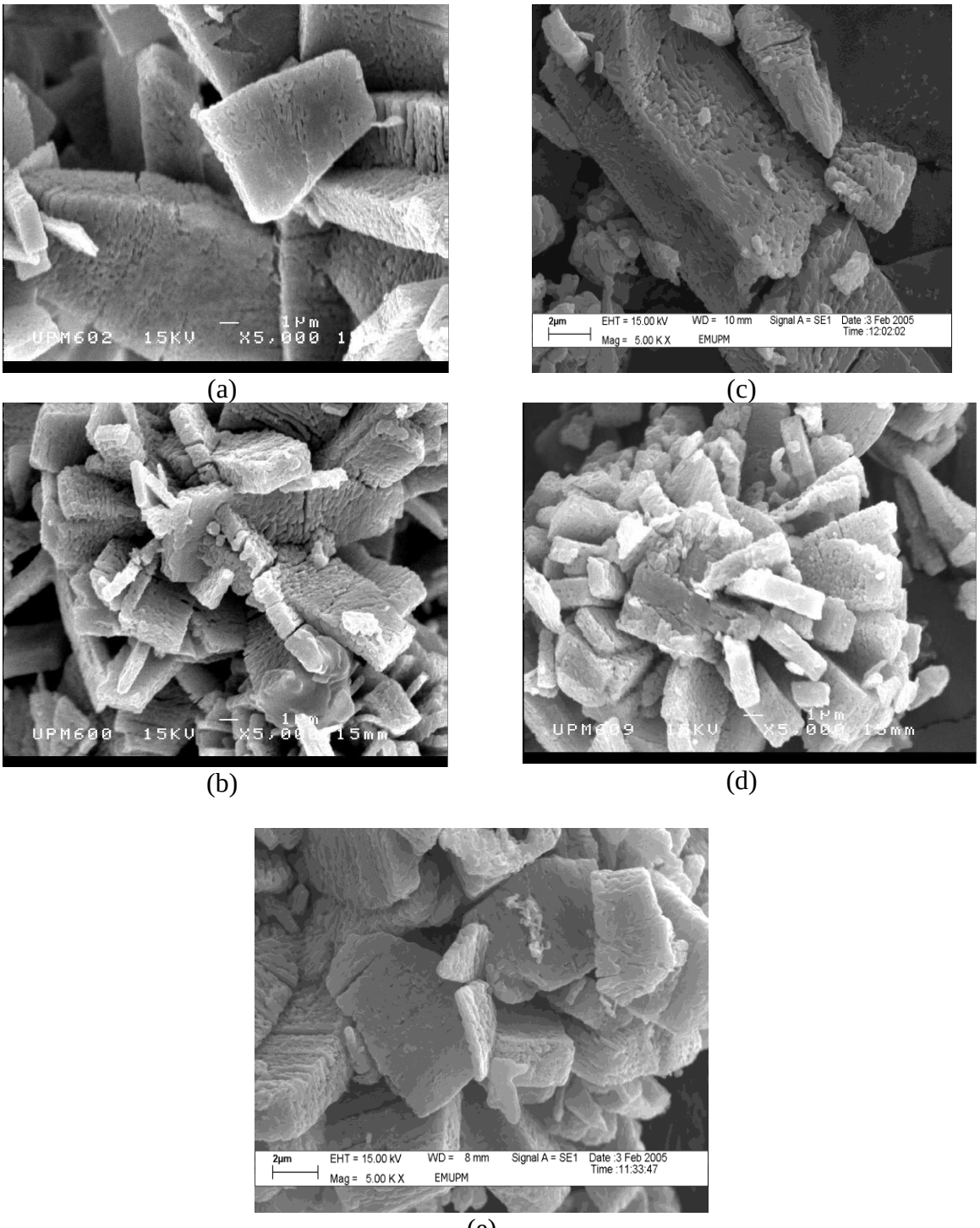

Figure 3: SEM images of V_2O_5 under magnification 5000X: (a) VO1, (b) VO2, (c) VO3, (d) VO4 and (e) VO5.

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CONCLUSION

Vanadium oxides were prepared by precipitating V^{5+} ion with NH_4^+ in increasing pH method. Once the precipitates were formed, study on the effect of number of washing was carried out. Characterizations carried out on precursors and on calcined samples revealed that no significant effect of number of washing on the phase formation. Heat treatment in air at 500 °C was successful transformed the samples into its oxides. SEM morphology revealed that all the samples were rectangular in shape with sharp edges. This shape was retained even after washing. S_{BET} analysis showed that unwashed samples give highest S_{BET} value compared to other samples. Peptization was considered to occur when samples were washed for a number of times for it allowed the superfine particles to come together to form bigger ones, thus the smaller S_{BET} value.

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