Effect of sonochemical synthesis on vanadyl phosphate dihydrate ($VOPO_4 \cdot 2H_2O$)

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Abstract

Six vanadyl phosphate dihydrate were prepared via sonochemical synthesis with different duration of time, *i.e.* 15, 30, 45, 60, 90 and 120 min are denoted as DS15, DS30, DS45, DS60, DS90 and DS120, respectively. All these samples were characterized by using X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). From the XRD patterns of the $VOPO_4 \cdot 2H_2O$ obtained via sonochemical synthesis at different time duration perfectly matched that of the standard $VOPO_4 \cdot 2H_2O$, indicating the high purity of the $VOPO_4 \cdot 2H_2O$ produced through this technique which drastically reduced the synthesis time to only 15 min instead of up to 24 h when compared to the conventional reflux method. The monographs obtained from SEM and TEM showed that DS120 produced a much more uniform plate-like structure and are stacked to each other to form a layered structure with diameters of ~1000nm.

Keywords: *sonochemical synthesis, vanadyl phosphate dihydrate, butane oxidation*

Introduction

Despite plentiful studies worldwide, progress in partial oxidation using catalysts has been hampered by low *n*-butane conversion and serious catalyst deactivation due to coke formation. It is well known that the preparation method of catalyst can affect the channel structure, the acid site density, and the oxidation state and location of the vanadium species. These are recognized factors which affect the catalytic performance of *n*-butane conversion. As a result an investigation of new methods of preparation and further optimization of catalyst performance was attempted.

It is believed the use of ultrasound irradiation can enhance the chemical reaction and mass transfer via the process of acoustic cavitation which will relatively shorten the time of VPO catalyst preparation and still display comparable oxidation activity for the liquid phase hydrogen peroxide oxidation of cycloalkanes in acetonitrile (Pillai, U.R., Sahle-Demessie, E. and Varma, R.S., 2003) In this study, the sonochemical synthesis technique was introduced where ultrasound irradiation to synthesize $VOPO_4 \cdot 2H_2O$ with different time duration were employed and its physico-chemical characteristics produced were then characterized by using x-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM).

Materials and Methods

Preparation of sonochemical synthesis of $VOPO_4 \cdot 2H_2O$

Vanadium pentoxide, V_2O_5 (2.0 g from Fluka), ortho-H_3PO_4 (32 cm^3, 85 % from Merck) and 100 cm^3 of distilled water were mixed inside 250 cm^3 beaker and exposed to high intensity irradiation under ambient air for 15, 30, 45, 60, 90 and 120 min. Ultrasound irradiation was accomplished with a high intensity ultrasound probe (2cm diameter Ti-horn, 20kHz, 500W) immersed directly in the reaction solution. The sonication was conducted without cooling so that the temperature of the reactant mixture increased gradually (~353 K) and the colour of the solid solution changed slowly from brownish to yellow.

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The resultant yellow solid ($VOPO_4•2H_2O$ phase), was then recovered by using centrifuge technique and subsequently washed sparingly with acetone and oven dried at 373 K for 24 h and denoted as DS15, DS30, DS45, DS60, DS90 and DS120.

Catalysts characterization

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.

Transmission Electron Microscope (TEM) is a powerful technique to study the structures at and below the nanometer scale. It allows a precise observation of nanostructures with an exceptional resolution (about 0.2 nm). Therefore, this technique is widely used to characterise nano-scale materials. The particle size of the samples was examined using LEO 912AB energy filter transmission electron microscope with an acceleration voltage of 120 kV.

Results and Discussions

X-ray diffraction (XRD)

The XRD patterns (Figure 1) of $VOPO_4•2H_2O$ obtained via sonochemical synthesis in different time duration perfectly matched that with the standard $VOPO_4•2H_2O$ (JCPDS File No. 36-1472). The main characteristic peaks at 2θ = 11.9°, 23.9° and 28.7° are corresponding to (001), (002) and (200) planes, respectively.

The sonochemical synthesis process with different time duration that produced vanadyl phosphate dihydrate, $VOPO_4•2H_2O$, basically did not cause any changes, in terms of the basic matrix of the $VOPO_4•2H_2O$phase as evidenced from the standard provided by the JCPDS. This further proved that no peaks of any other phases were detected indicating the high purity of the $VOPO_4•2H_2O$ produced through this synthesis technique which drastically reduced the synthesis time to only 15min instead of up to 24h when compared to the conventional reflux method.

Scanning Electron Microscope (SEM)

Figure 2 shows the SEM micrograph of$VOPO_4•2H_2O$ prepared through conventional reflux method. The morphology of $VOPO_4•2H_2O$ produced consist of large platelet particles that are stacked to each other to form layered material. This is in agreement with the results obtained by other researchers (Hiyoshi, N. et al., 2004; Yamamoto, N. et al., 2002; Nakato, T. et al., 2000). The morphologies of $VOPO_4•2H_2O$ produced which were subjected to the sonochemical synthesis technique are shown in Figure 3. The microstructure of the $VOPO_4•2H_2O$ obtained through this technique are smaller with irregular shape compared to the conventional method. However, that which was subjected for 120 min ***(Figure 3f)*** produced a much more uniform plate-like structure and was stacked to each other to form a layered structure

Transmission Electron Microscope (TEM)

The particle size synthesised with different time duration were examined by using transmission electron microscope ***(Figure 4)***. The TEM images showed that the sonochemical synthesised $VOPO_4•2H_2O$ consist of sub-micron particles with diameters of 420-1060 nm compared to that prepared through the conventional method whose particle sizes was about 0.1-0.3 mm (Park, N.G. et al., 2001). The TEM images from this investigation also further confirmed that the sub-micron particles are unstable and tend to agglomerate with each other to form larger particle. However, the sonochemical synthesis technique is able to produce $VOPO_4•2H_2O$ sub-micron particles within few minutes compared to the conventional reflux method.

Conclusions

All the $VOPO_4•2H_2O$ produced through

sonochemical synthesis at different durations produced no peaks of any other phases indicating the high purity of the $VOPO_4 \cdot 2H_2O$ obtained and which also reduced the synthesis time to only 15min rather than up to 24h when compared to the conventional reflux method. In addition, the $VOPO_4 \cdot 2H_2O$ that was subjected for 120min produced a much more uniform plate-like structure with diameter of ~1000nm and was stacked to each other to form a layered structure.

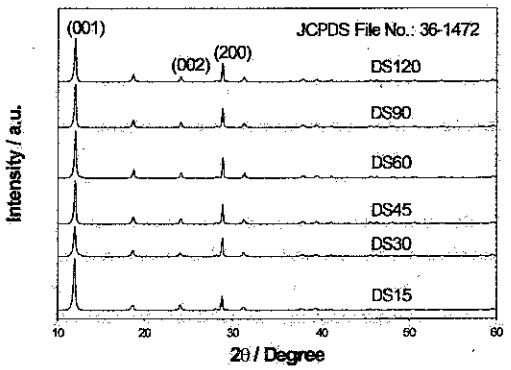


Figure 1: *XRD patterns of sonochemical synthesised anadyl phosphate dihydrate (DS15-DS120)*

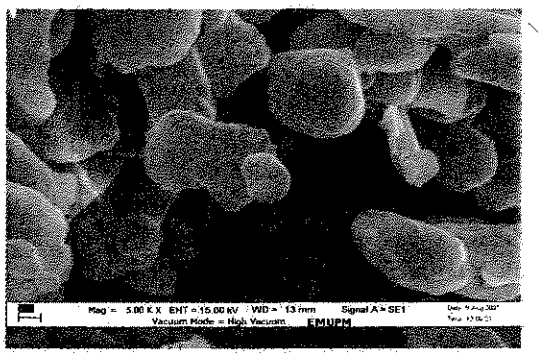
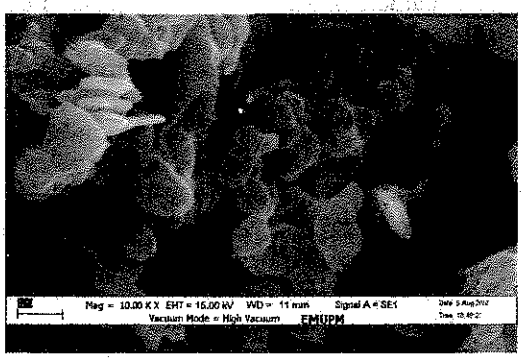
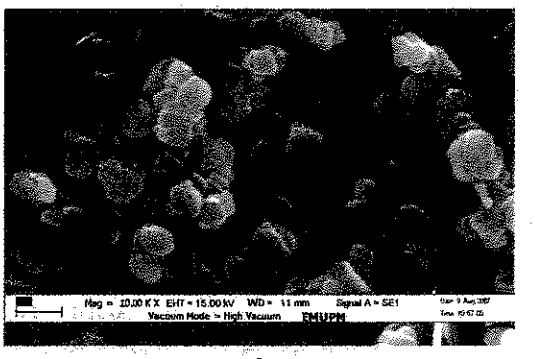


Figure 2: *SEM micrograph of VOPO4 (with 10000x magnification)*

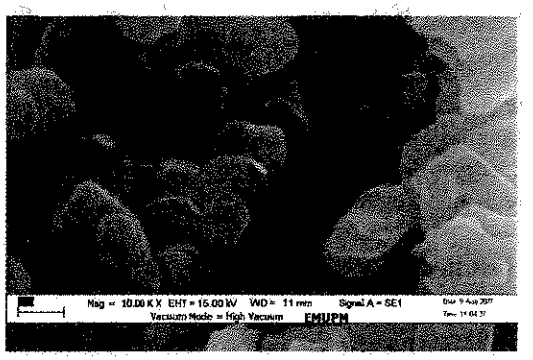


(a)

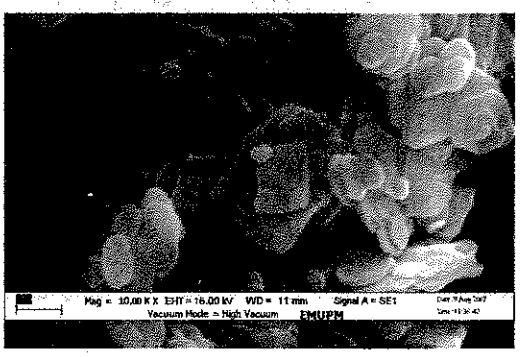


(b)

(c)



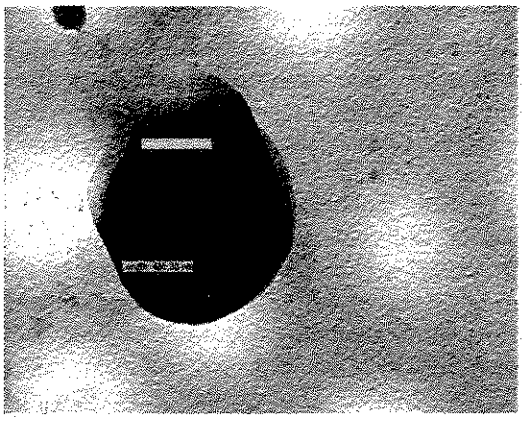
(d)



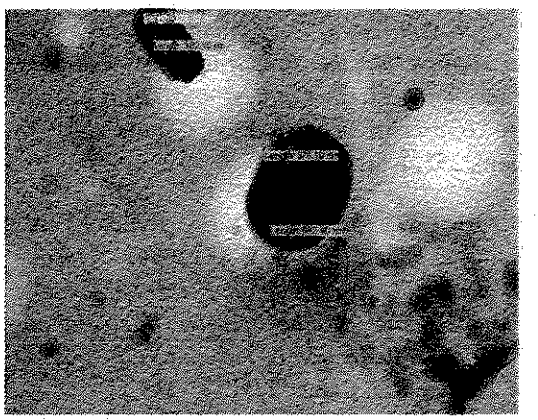
(e)

(f)

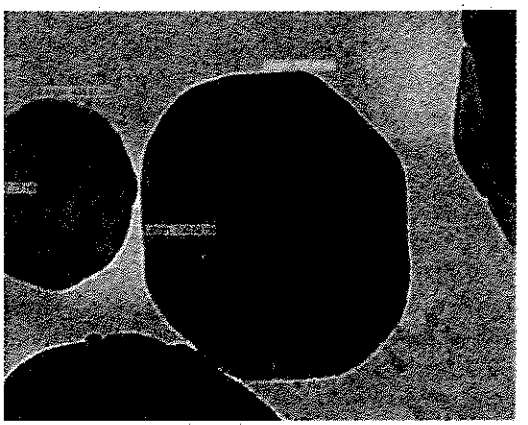
Figure 3: *SEM micrograph of (a) DS15, (b) DS30, (c) DS45, (d) DS60, (e) DS90 and (f) DS120 (with 10000× magnification)*



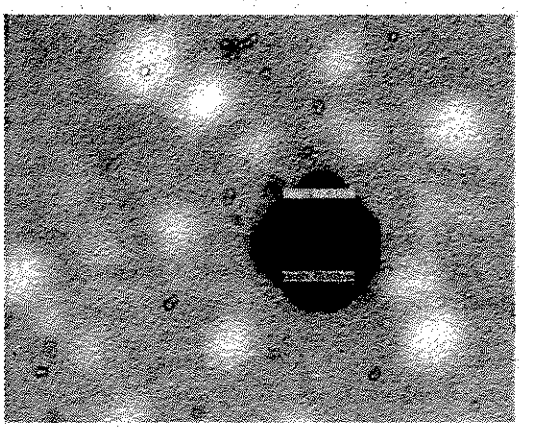
(a) ~500 nm



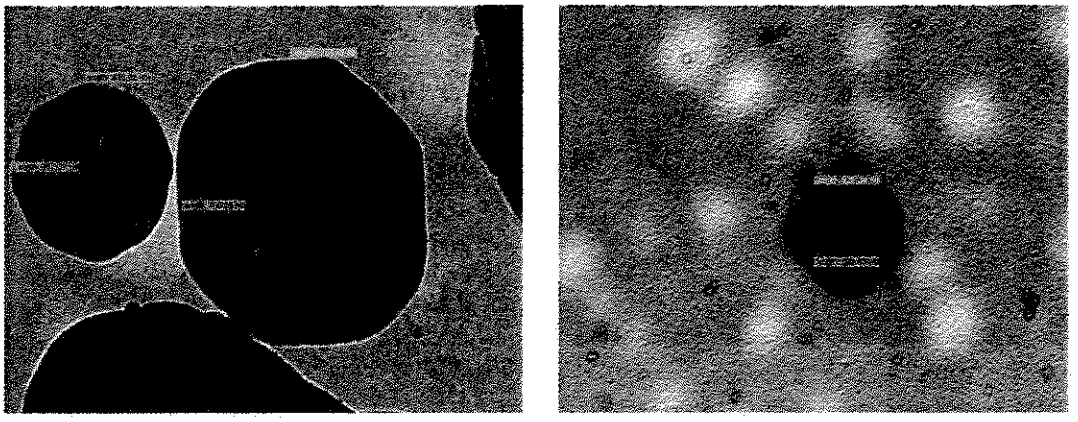
(b) ~400 nm



(c) ~450 nm



(d) ~1000 nm



(e) ~700 nm *(f) ~1000 nm*

Figure 4: *TEM micrograph of (a) DS15, (b) DS30, (c) DS45, (d) DS60, (e) DS90 and (f) DS120*

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