

Properties and catalytic performance of sulphate-vanadia impregnated fumed silica as oxidative catalyst

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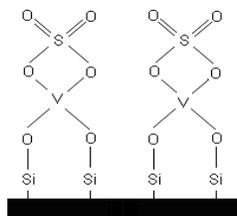
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GRAPHICAL ABSTRACT



ABSTRACT

A series of sulphate-vanadia impregnated fumed silica oxidative catalysts were synthesized via impregnation method. The samples were prepared by impregnating 1 wt% of vanadium and 0.2 M of sulphuric acid onto fumed silica support. Surface area of all the silica supported samples was approximately 118 m²/g. UV-Vis DRS results showed the existence of supported V species and charge transfer bands associated with O²⁻ to V⁵⁺ in tetrahedral environments. Catalytic performance was evaluated via epoxidation of 1-octene to 1,2-epoxyoctane using hydrogen peroxide as oxidant. It had been demonstrated that sulphate-vanadia impregnated fumed silica had high catalytic activity where 626 ± 0.2 mmol epoxide was produced after 24 h reaction. The results implied that more oxidative sites were generated after the impregnation of V and sulphate onto the SiO₂ matrices.

Keywords: Oxidative catalyst, Vanadia, Sulphate, Fume silica

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1. INTRODUCTION

Epoxides are valuable and versatile commercial intermediates. They are highly reactivity due to the highly opening strained three-membered ring [1]. Apparently, the epoxides turn out to be very important chemical products for synthesis of other materials in the fine chemical industry. Therefore, many works have been done to enhance the epoxide selectivity because of the importance of epoxides in the synthesis of organic and pharmaceutical materials.

Titania and TiO₂-based materials have been reported as the most effective oxidation catalysts for various reactions, including olefin epoxidation [2,3]. Amongst, titanium-containing silicalite, TS-1 was an excellent oxidative catalyst due to presence of tetrahedrally coordinated titanium in a silicate structure [4].

Recently, an oxidative-acidic bifunctional catalyst was synthesized by impregnation of 1 wt% vanadium onto silica-titania aerogel [5]. It was reported that both titania and vanadium responsible in the formation of oxidative sites on the surface of the catalyst. However, the competition between titania and vanadium as oxidative catalyst could have reduced the catalytic efficiency of the material, hence making their roles unclear.

In this work, a titania free oxidative catalyst of sulphate-vanadia supported on silica was prepared. The

role of the vanadium as oxidative site was reexamined. Besides, effectiveness of fumed silica, a relatively cheap silica material as catalyst support was investigated.

2. EXPERIMENTS

2.1 Synthesis of catalyst

Synthesis of sulphate-vanadia loaded onto fumed silica (Merck) was prepared via wet impregnation method at room temperature. Vanadia (1 wt%) was dissolved in 25 mL of distilled water and impregnated with 2.0 g of SiO₂. The mixture was stirred for 1 h, dried overnight at 373 K and finally calcined at 823 K for 7 h. Subsequently, the catalysts were further modified with 0.2 M sulphuric acid via wet impregnation method. The final resulted material was labeled as HS/V/SiO₂.

For comparison purpose, materials were also prepared via different synthesis methods and loading sequences in order to create dissimilar interaction among the elements in the materials. A mixture of 2.0 g SiO₂ and 25 mL of 0.2 M sulphuric acid was stirred vigorously at room temperature for 1 h. Later, the mixture was dried at 373 K for overnight and followed by calcinations at 823 K for 7 h. Subsequently, 1 wt % V₂O₅ was loaded onto SiO₂ via wet impregnation method. The loading process used

was similar to that of synthesis procedure of HS/V/SiO₂. The resulted material was labeled as V/HS-SiO₂.

On the other hand, 1 wt% of V was dissolved with 25 mL of 0.2 M sulphuric acid. The solution was impregnated to the 2.0 g of SiO₂. The process was continued with dried at 373 K for overnight and followed by calcinations at 823 K for 7 h. The resulted material was denoted as V-HS/SiO₂.

2.2. Characterization

The crystallinity and phase purity of the samples were identified by X-ray diffraction (XRD), using a Bruker Advance D8 using Siemens 5000 diffractometer with the Cu K α ($\lambda=1.5405 \text{ \AA}$) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. The spectra was scanned in the 2θ range between 2° and 30° at a step 0.050° and step time 1 s. Diffused reflectance UV spectra were under ambient condition using a Perkin Elmer Lambda 900 DRUV/VIS spectrometer over range from 190 to 800 nm. The surface area was determined by means of BET N₂ adsorption using Quantachrom surface area analyzer. The analyzer was calibrated using Al₂O₃ as the standard material prior to analysis. On the other hand, infrared measurements were performed on a Perkin Elmer Spectrum One FT-IR spectrometer, with a spectral resolution of 2 cm^{-1} , scan time of 10 s using the KBr pellet technique. The framework spectra were recorded in the region of $400 - 4000 \text{ cm}^{-1}$.

2.3 Catalytic testing

The catalytic testing of the samples was evaluated through the epoxidation of 1-octene using aqueous H₂O₂ as oxidant. The reaction mixture containing of 8 mmol of 1-octene (Fluka, 97%), 8 mmol of H₂O₂ in H₂O (Qrec, 30%) in 10 mL acetonitrile (J.T beaker) as solvent and 70 μL of cyclohexane (Fluka, 99%) as the internal standard was placed in a round bottom flask equipped with magnetic stirrer and condenser. About 0.05 g catalyst was added into the solution. The reaction was carried out in oil bath at 343 K for 24 h under stirring condition. The products of the reaction were analyzed on a HP Agilent 6890N gas chromatograph using Ultra-1 column.

3. RESULTS AND DISCUSSION

3.1 Physical Appearance

All the samples were light and fluffy powder. The colour of all sulphate-vanadia doped samples changed from blue to green colour after calcination at 823 K for 7 h. It was suggested that, during this step V in these samples has changed from V(IV) toward a higher oxidation state of V(V). Similar observation was reported previously [5].

3.2 Characterizations

Fig. 1 shows the X-ray diffractograms of the prepared samples. The amorphous structure of SiO₂ remained after impregnation and calcinations processes as indicated by the broad and featureless X-ray diffractograms. The absence of peaks in the diffractograms further suggested that no diffraction lines for sulphate or vanadia. The results may imply that both sulphate and vanadia are highly dispersed on the surface of SiO₂. Alternatively, the broad and featureless X-ray diffractograms could be attributed to the low content of vanadia in the samples.

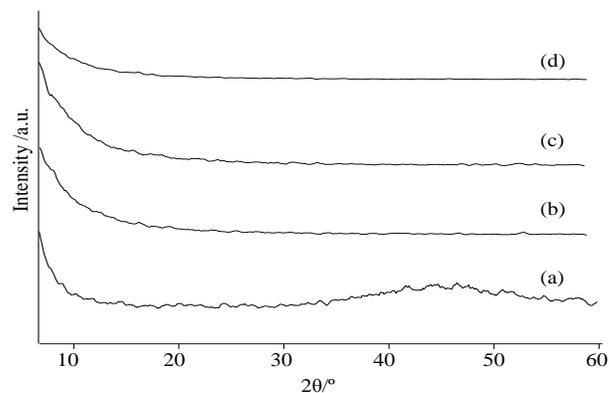


Figure.1 X-ray diffractograms of (a) SiO₂, (b) V/HS-SiO₂, (c) HS/V/SiO₂ and (d) V-HS/SiO₂

Table 1 shows that all the samples are having surface area in range $118-150 \text{ m}^2/\text{g}$. The high surface area fume SiO₂ ($150 \text{ m}^2/\text{g}$) was used as catalyst support. As observed, a significant decrease of $\sim 21\%$ in surface area was observed after impregnation of V and H₂SO₄ onto SiO₂. The usage of SO₄²⁻ group would have led to coalescence process during calcinations, bringing to partial destruction of the SiO₂ structure [6,7].

Table.1 Surface area and pore volume of the samples

Samples	Surface area (m^2/g) $\pm 5\%$
SiO ₂	150
V/HS-SiO ₂	118
HS/V/SiO ₂	118
V-HS/SiO ₂	119

UV-Vis DRS spectra of all the samples are depicted in Fig. 2. Generally, two bands at around 250 nm and 380 nm were detected in the samples. Absorption band in range 250-300 nm is attributed to the charge transfer transitions between tetrahedral oxygen ligands and the framework-substituted V⁵⁺ ions, while the band at 350-400 nm corresponds to V species on the wall surfaces [7] due to the charge transfer (CT) bands associated with O²⁻ to V⁵⁺ in tetrahedral (Td) environments. As can be seen in Fig. 2, sample HS/V/SiO₂ exhibited a more intense band at 250 nm and 380 nm compared to other samples, implying this sample may consist of more V⁵⁺ species. However, the synthesis methods did not give significant impact on the type of V species generated in the samples.

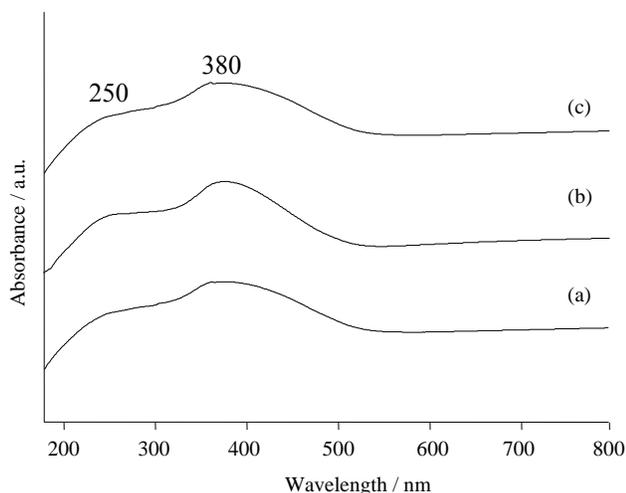


Figure.2 UV-Vis spectra of (a) V/HS-SiO₂, (b) HS/V/SiO₂ and (c) V-HS/SiO₂

FTIR spectra of samples show typical silicate absorptions at 466 and 1100 cm⁻¹ which were attributed to Si-O-Si bending and stretching vibrations, respectively [10, 11] (Fig. 3). The band at 799 cm⁻¹ was associated with absorptions of Si-O-V, which also correspond to transition metal bonding. Obviously, the sample V/HS-SiO₂ has the least Si-O-V bondings. It is believed that the direct sulfuric acid treatment had brought to significant alteration on the surface of silica, resulting in limited formation of Si-O-V bondings. On the other hand, OH group bands were observed at 1650 and 3400 cm⁻¹. Besides, no band matching to H₂SO₄ was identified. This may be due to its low concentration used in the impregnation process and low vibration intensity of SO₄²⁻ itself.

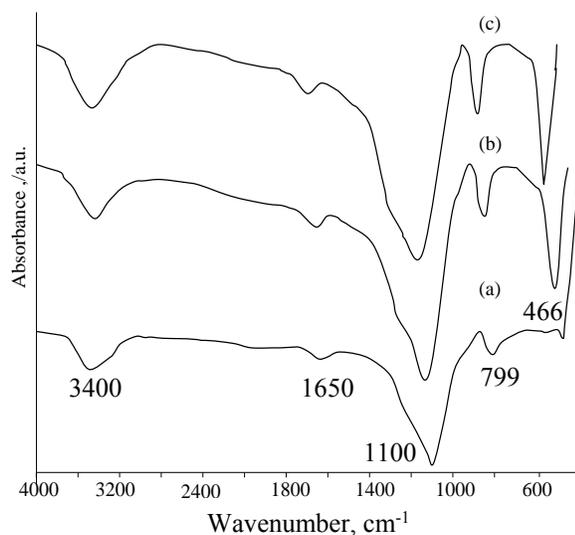


Figure.3 FTIR spectra of (a) V/HS-SiO₂, (b) HS/V/SiO₂ and (c) V-HS/SiO₂

3.3. Catalytic Testing

The catalytic properties of all the samples were studied in the epoxidation of 1-octene using H₂O₂ as oxidant in acetonitrile as solvent at 343 K. After loading of V and sulphuric acid, the samples has remarkably enhanced catalytic activity in oxidation reaction to form 1,2-epoxyoctane. As shown in Table 2, the sample HS/V/SiO₂ had the highest yield of 1,2-epoxyoctane (626 ± 0.2 mmol), followed by sample V/HS-SiO₂ (24 ± 0.4 mmol). Since the V species is widely recognized as the active site for epoxidation reaction [11], the excellent oxidative catalytic activity of these samples could be closely associated to the existence of this V species in these samples as evidenced in UV-Vis DRS results.

Table.2 Yield of the product of the samples

Sample	Yield of product (mmol) 1,2-epoxyoctane
SiO ₂	0
V/HS-SiO ₂	24 ± 0.4
HS/V/SiO ₂	626 ± 0.2
V-HS/SiO ₂	0

As compare to V₂O₅ impregnated onto SiO₂-TiO₂ [5], epoxide yield of the sample HS/V/SiO₂ was 13 time higher than that of V₂O₅ impregnated onto SiO₂-TiO₂. It may be attributed to presence of sulfuric acid which has strengthened the oxidative activity of the sample. Whereas sample V-HS/SiO₂ has no detected yield of 1,2-epoxyoctane due to different approach in synthesis procedure resulting in insufficient of oxidative sites.

It is known that 1,2-epoxyoctane will be further converted to 1,2-octanediol if Brönsted acidity is available in the samples (Fig. 4). It was reported that the direct interaction between PO₄³⁻ and V₂O₅ or PO₄³⁻ and Nb₂O₅ contributed to formation of Brönsted acidity [5,12]. However, our current research showed that there was no detection of any 1,2-octanediol after 24 h of reaction in all samples, strongly suggesting absence of Brönsted acid sites in the samples for the transformation of diol. Therefore, it is believed that, V⁵⁺=O at surface might have performed as oxidative sites in the reaction, without involving in generation of Brönsted acid sites. This phenomenon implied that co-existence of sulphate group and V₂O₅ does not produce Brönsted acidity. It is noteworthy that a relatively economical support of SiO₂ was used to produce an oxidative catalyst in this work.

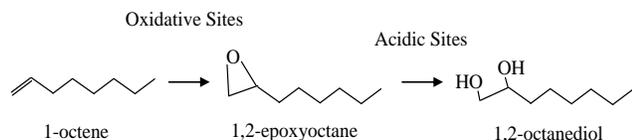


Figure.4 Reaction scheme showing the transformation between 1-octene, 1,2-epoxyoctane and 1,2-octanediol.

4. CONCLUSION

Oxidative catalyst of sulphate-vanadia impregnated fume silica was synthesized by simple wet impregnation method. The catalytic testing results showed that HS/V/SiO₂ was an excellent oxidative catalyst in the epoxidation of 1-octene to 1,2-epoxyoctane. This sample showed high yield of 1,2-epoxyoctane (626 ± 0.2 mmol) after 24 h reaction. Synthesis method of impregnation of V into SiO₂, followed by sulphuric acid has led to the formation of more oxidative sites in the sample, resulting in better performance of catalytic activity compared to the others. It had been demonstrated V⁵⁺ played important roles as oxidative sites for 1-octene epoxidation and fumed silica served as a potential support for oxidative catalyst.

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