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Abstract

Enhancement of Brønsted acidity in silica-titania aerogel was achieved by loading both sulfate and vanadium onto the material. This phenomena could be due to formation of $V(OSi)_2OH\text{-}O\text{-}SO_3^-$ in the resulted sample. In contrast, no noticeable Brønsted acidity was detected in vanadium loaded silica-titania aerogel (V/ST). UV-vis DR analysis results showed that the amount of hydrated tetrahedral titanium species, which acts as oxidative site, increased significantly upon sulfation and vanadium loading on the surface of the aerogel. However, presence of vanadium in the samples tended to transform framework tetrahedral titanium to extra framework octahedral titanium structure. The catalytic performance of the samples were evaluated in consecutive transformation of 1-octene to 1,2-octanediol through formation of 1,2-epoxyoctane using aqueous H_2O_2.

KEYWORDS: silica-titania aerogel, Brønsted acid, sulfate, vanadium, impregnation, bifunctional catalyst

Introduction

A bifunctional catalyst is potentially active for consecutive processes as it consists of two active sites in a single material. The catalyst, therefore, could be a promising catalyst in production of diols which currently are manufactured industrially via a two-step sequence consisting of epoxidation of an olefin, followed by hydrolysis of the resulting epoxides. It has been demonstrated that sulfated zirconia loaded TS-1 consisted of oxidative site attributed to titanium located in the framework of silicalite, while octahedral zirconia containing sulfate as Brønsted acidic sites. The bifunctional catalyst led to a consecutive transformation of 1-octene to 1,2-octanediol though formation of 1,2-epoxyoctane (Prasetyoko *et al*., 2005). However, limited Brønsted acidity in the sample has restricted the production of diols.

Owing to their high surface area and larger porosity, the mesoporous materials have been used widely as support in the catalyst modification (Kresge *et al.*, 1992; Hamdan *et al*., 2009). Generation of Brønsted acid sites in mesoporous materials were found in sulfated Al-MCM41 and phosphate-impregnated MCM-41 (Poh *et al*., 2006; Kawi *et al*., 2002). Nevertheless, no any oxidative site was available on MCM-41 based materials. Silica-titania aerogel, however, is an excellent catalyst for epoxidation due to the highly distribution of Ti^{4+} species in the catalyst (Müller *et al*., 2000; Hu *et al*., 2003). Unfortunately, no any Brønsted acidity was detected in silica-titania aerogel, but only Lewis acidity (Hu *et al*., 2003). Recently, we have demonstrated the formation of Brønsted acid sites in sulfated silica-titania aerogel and it was an excellent oxidative and acidic bifunctional catalyst in a consecutive reaction (Ling *et al*., 2008).

On the other hand, an increase in the number of Brønsted acid sites was found when vanadia was supported on a metal oxide (Datka *et al*., 1992). Deposition of vanadium on silica, titania and silica-titania aerogel also tend to increase the amount of both Brønsted and Lewis acidity (Reicher *et al*., 1999). In this work, an attempt was made to further increase Brønsted acidity by introducing both sulfate group and vanadium onto silica-titania aerogel. The effect of co-existence of sulfate and vanadium on physiochemical properties and catalytic performance of silica-titania aerogel was studied.

Experimental

(i) Synthesis of Bifunctional Catalyst

Silica-titania aerogel (molar ratio of Si:Ti=33:1) and sulfated silica-titania aerogel were prepared according to a procedure described earlier in our previous work (Ling *et al*., 2008). Impregnation of 1 wt% of vanadium onto silica-titania aerogel

(ST) was carried out by dissolving the necessary amount of vanadyl sulfate hydrate (VOSO$_4$.H$_2$O, Fluka) in H$_2$O. Meanwhile, sulfate-vanadium loaded silica-titania aerogel was prepared by adding vanadyl sulfate hydrate into 25 mL of 0.2 M sulfuric acid solution. The mixture was stirred vigorously at room temperature for 2 h, followed by drying at 100°C for 2 days. The obtained solid was ground and followed by calcination at 500°C for 7 h.

(ii)   Characterization

A Qsurf surface area analyzer was used to characterize surface area and pore volume of the calcined samples. The powder X-ray diffraction (XRD) analysis by means of a Bruker Advance D8 equipped Siemens 5000 diffractometer with the Cu K$_\alpha$ (λ = 1.5405 Å) radiation was carried out for crystallinity determination of the samples. XRD analysis was carried out at a step of 0.02^o and step time 1 s over 2θ range of 2° to 50° with the diffracted monochromatic beam at 40 kV and 40 mA. Diffused reflectance UV spectra were collected under ambient conditions using a Perkin Elmer Lambda 900 DRUV/VIS/NIR spectrometer over the range from 190 to 800 nm. Infrared measurements, with a spectral resolution of 2 cm^{-1}, scan time of 10 s using the KBr pellet technique were performed on a Perkin Elmer Spectrum One FT-IR spectrometer. For acidity study, the wafer of sample (~14 mg) was locked in the cell equipped with CaF$_2$ windows and evacuated at 200°C under vacuum condition for 3 h. Infrared spectra of the sample were recorded at room temperature after desorption of pyridine at 150°C for 1 h. The types of acid sites were examined using pyridine as a probe molecule.

(iii)   Catalytic Testing

The catalyst activity of sulfate and vanadium modified silica-titania samples was evaluated through the epoxidation of 1-octene using aqueous H$_2$O$_2$ as oxidant. The reaction mixture containing 1-octene (8 mmol, Fluka, 97%), H$_2$O$_2$ (15 mmol, Hanns, 35%), acetonitrile (10 mL, J.T. Baker) as solvent and 100 μL of cyclohexanon (Merck, extra pure) as the internal standard was put in a round bottom flask equipped with a condenser. 0.050 g of the catalyst was then added to the solution. The reaction was carried out in an oil bath under stirring at 70°C for 24 h. Finally, the products of the reaction were analyzed using a GC-MS and GC. Calibration curves for potential products were plotted. Amount of products yielded was calculated from ratio of peak area of product to that of internal standard. Three set of experiments were carried out for each catalyst.

Results and Discussion

(i)   Physical Properties

Silica-titania aerogel (ST) and sulfated silica-titania aerogel (SO$_4$/ST) were light fluffy powder and semi-transparent even after the 500°C calcination step in air. Colour changing was observed in the vanadium loaded samples: V/ST changed from white to yellow; while SO$_4$_V/ST appeared in pale green after calcination due to shifting of vanadium toward a higher oxidation state (Wang *et al*., 2004).

(ii)   Characterization

As shown in Table 1, the loading of sulfate groups has given a greater impact to the surface area of silica-titania aerogel than that of vanadium loading (7% loss). The 30% and 16% loss observed in SO$_4$/ST and SO$_4$_V/ST, respectively, could be associated to a coalescence process in the presence of acid during calcinations. Unlike sulfate group, usage of phosphate group in modification of silica-titania aerogel led to a complete destruction of the aerogel structure (Lee *et al*., 2009). It is widely accepted that higher surface area plays a key role for better catalytic activity as it allows more reaction between reactant and catalyst. No significant change in pore volume after sulfate loading was observed, indicating that sulfate groups were well dispersed on the silica-titania sample. However, the pore volume of silica-titania aerogel increased with addition of vanadium. This phenomenon could be attributed to the presence of vanadium during the impregnation process has changed the ionic strength of the gel, resulting in the formation of a bigger pore as well as a lower surface area (Davydov *et al*., 2001).

Table 1. BET surface area and pore volume of ST and sulfate-vanadium modified ST catalysts

Catalyst	Surface area (m^2/g) $\pm$ 5%	Pore volume (cm^3/g) $\pm$ 5%
ST	550	0.98
SO$_4$/ST	384	0.96
V/ST	511	1.09
SO$_4$_V/ST	462	0.95

No peak was observed in the X-ray diffractograms of the samples, indicating that the amorphous structure of aerogel remained after impregnation and calcinations process (Figure 1). The broad and featureless X-ray diffractograms further implies Ti and V were highly dispersed on the surface of silica aerogel, or were incorporated into silica framework. It also suggested that Ti presents neither in anatase nor rutile form. Nevertheless, it could also be attributed to the low content of Ti and V in the synthesized samples.
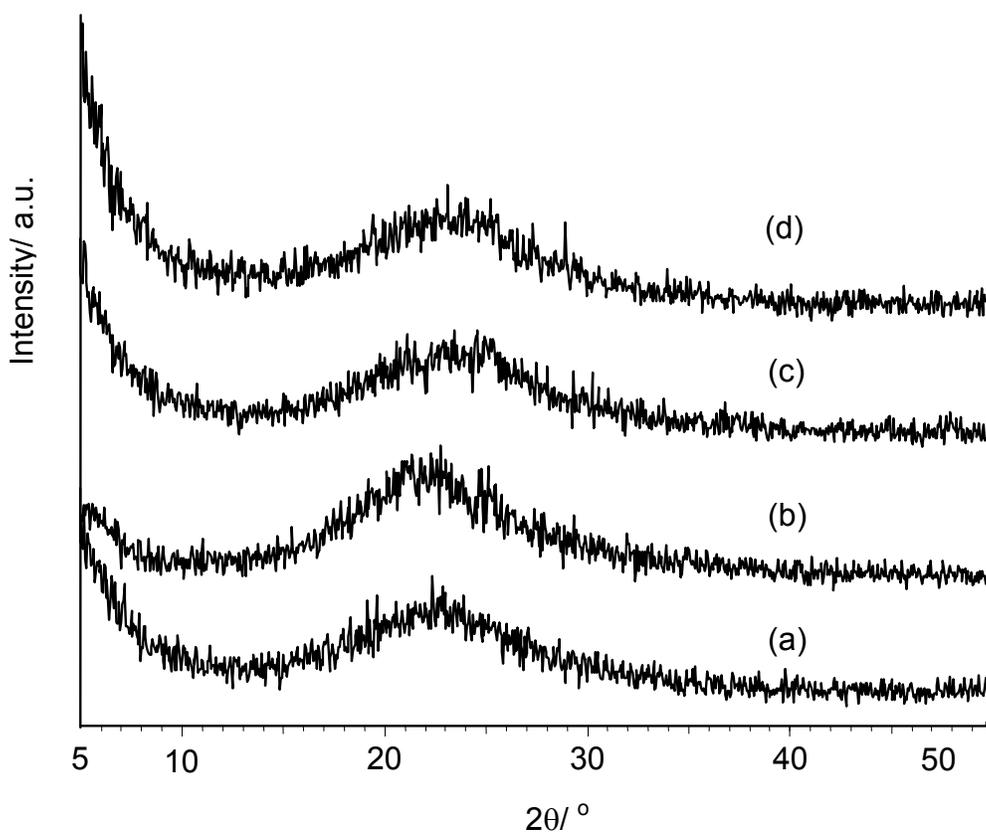

Figure 1: XRD patterns of ST and sulfate-vanadium modified ST samples: (a) Silica-titania aerogel (ST); (b) sulfated silica-titania aerogel (SO_4/ST); (c) vanadium loaded silica-titania aerogel (V/ST); and (d) sulfate-vanadium modified silica-titania aerogel (SO_4_V/ST).

As shown in the DRUV-Vis spectra (Figure 2), three absorption bands at 210, 250 and 296 nm are observed in those treated samples. Apparently, an intense band at 250 nm associated with hydrated tetrahedral titanium species was

found in samples SO$_4$/ST, V/ST and SO$_4$_V/ST. The results strongly suggest that the amount of hydrated tetrahedral titanium species on the surface of the aerogel has increased significantly upon sulfation and vanadium loading (Ling *et al*., 2008). The band at 296 nm that attributed to the octahedrally coordinated or polymetric titanium species was obviously detected in those vanadium loaded samples, indicating presence of vanadium in the samples favored transformation of framework tetrahedral titanium to extra framework octahedral titanium structure. Similar transformation was reported in sulfated TS-1 (Nur *et al*., 2004). On the other hand, the shoulder band at 210 nm was attributed isolated, tetrahedral titanium species. This electronic transition that assigned to a charge-transfer of the tetrahedral titanium sites between O^{2-} and central Ti(IV) atoms (Zecchina *et al.,* 1996) was clearly observed especially in sample SO$_4$_V/ST. It strongly implies that co-existence of vanadium and sulfate group in the sample tends to convert titanium species into three different types: isolated tetrahedral, hydrated tetrahedral and octahedral coordinated titanium species. Both vanadium loaded samples of V/ST and SO$_4$_V/ST exhibited a broad band between 400-500 nm which was attributed to vanadium species.

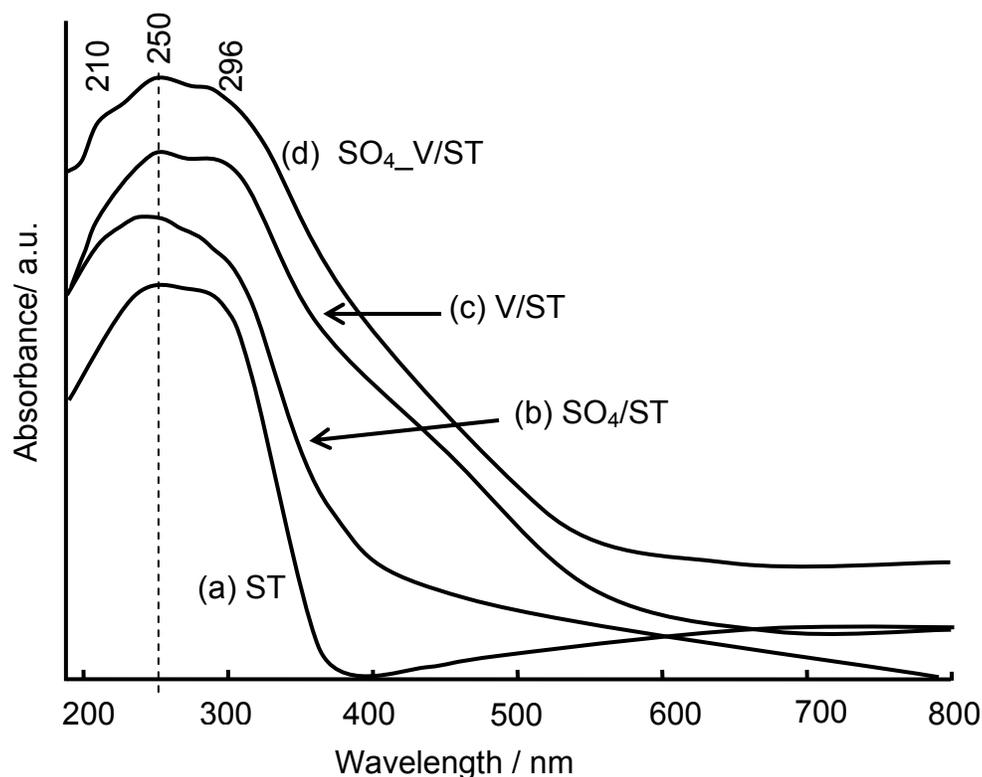Figure 2: DRUV-Vis spectra of (a) ST; (b) SO$_4$/ST; (c) V/ST; and (d) SO$_4$_V/ST.

FTIR spectra of ST, sulfate and/or vanadium treated ST samples show typical silicate absorptions at 1099 cm^{-1} and 468 cm^{-1}, attributed to Si-O-Si bending and stretching vibrations (Figure 3). The bands at 800 cm^{-1} and 963 cm^{-1} for sample ST shifted to higher wavenumbers after the treatment, implying the loading of sulfate and vanadium onto ST has weakened Si-O-Ti and Si-O-Si bonds. Accordingly, longer bond lengths were formed and hence decreased the force constant of the bonds in samples SO$_4$/ST, V/ST and SO$_4$_V/ST. No bands corresponding to sulfuric acid and vanadium were detected, may be due to their low concentration used in the impregnation process.
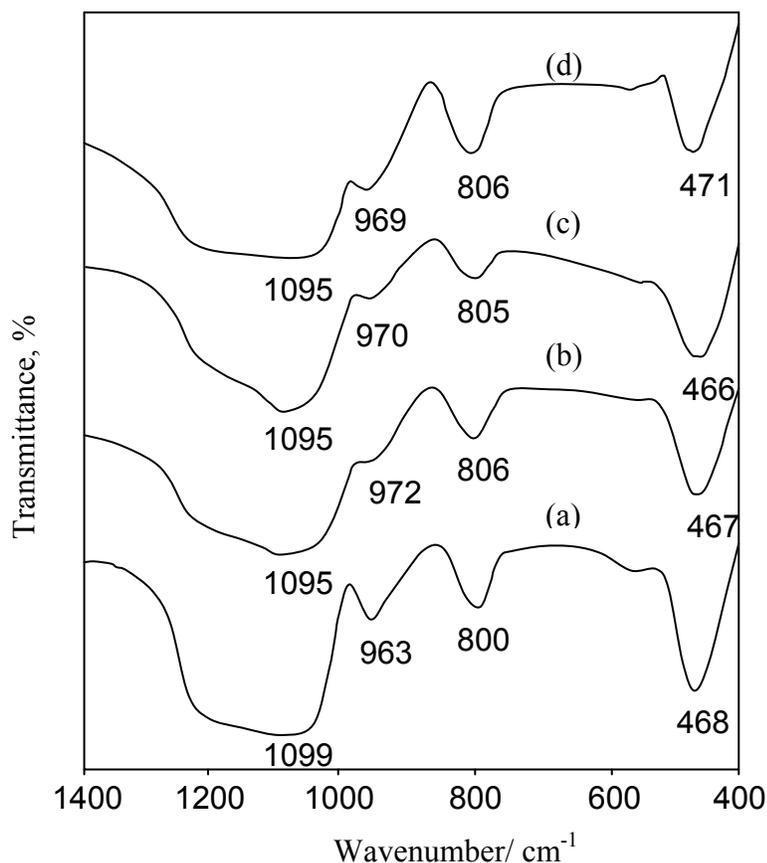

Figure 3: FT-IR spectra of (a) ST; (b) SO$_4$/ST; (c) V/ST; and (d) SO$_4$_V/ST

(iii)   Acidity

The hydroxyl groups and acidity of the samples were determined by infrared technique. The wafer sample was put in the glass cell and evacuated at 200°C for

3 h under vacuum, followed by pyridine adsorption at room temperature for 1 minute. Figure 4 shows the FTIR spectra of the ST and sulfate and/or vanadium treated ST samples after evaluation at 150°C for 1 h after pyridine adsorption. In the region of hydroxyl group (Figure 4(i)), the peak at 3744 cm^{-1}; assigned to silanol hydroxyl groups, was increased remarkably after loading of sulfate and vanadium. This observation further supports the finding obtained by DRUV-Vis study that there was a rise in hydrated tetrahedral titanium species amount in those sulfate and vanadium loaded samples, resulting in higher hydrophilic property. Meanwhile, the peak at 1400 cm^{-1}; assigned to asymmetric vibration of sulfonyl group, was seen in sulfated samples of SO$_4$/ST and SO$_4$_V/ST (Rosenberg *et al.*, 2003).
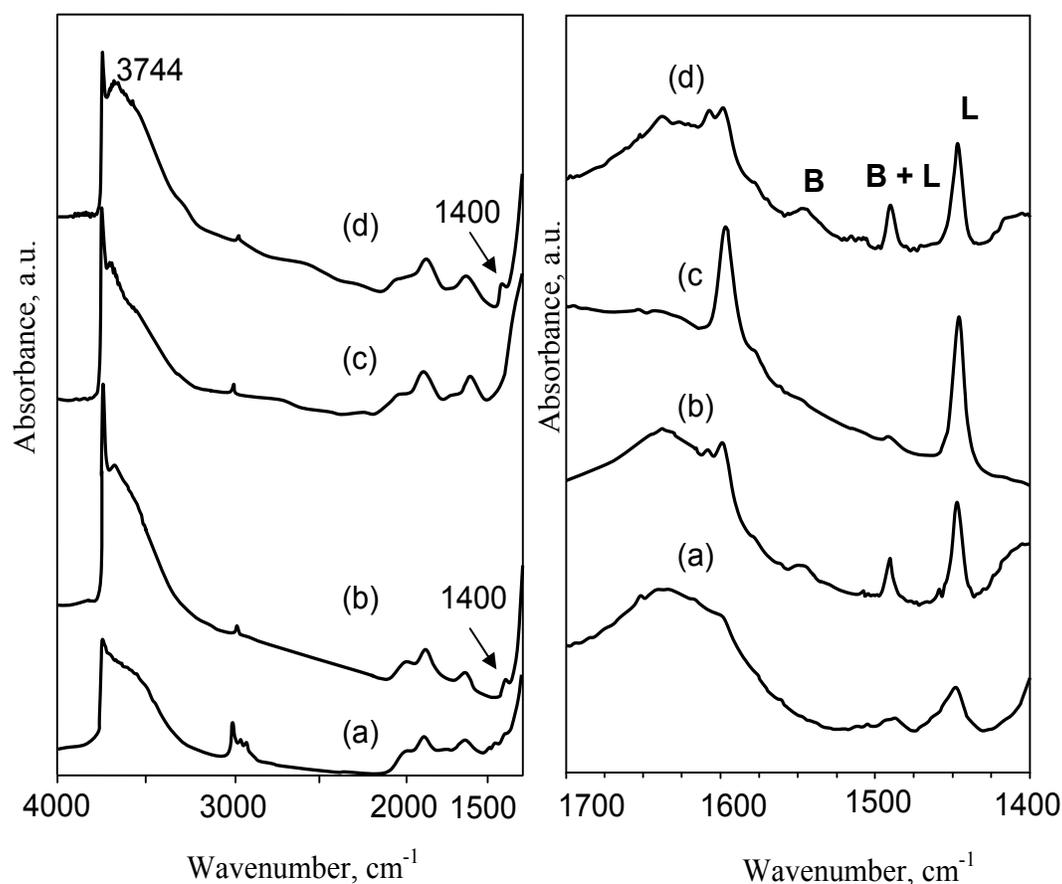

Figure 4: The pyridine –FTIR spectra of (a) ST; (b) SO$_4$/ST; (c) V/ST; and (d) SO$_4$_V/ST after (i) evacuation at 300°C for 3 h in vacuum, (ii) pyridine adsorption and evacuation at 150°C for 1h showing the presence of Lewis acid (L) and Brønsted acid (B) sites.

Figure 4(ii) illustrates infrared spectra of the samples in the pyridine region. The spectrum of ST showed the adsorption bands at 1600 cm^{-1} and 1446 cm^{-1} which are corresponding to pyridine interacting with Lewis acid sites. It strongly indicates that only limited amount of Lewis acid existed in silica-titania aerogel, agrees with previous report (Hu *et al*., 2003). Formation of both Lewis and Brønsted acidity in SO$_4$/ST had been discussed previously (Ling *et al.,* 2008). The amount of both Lewis and Brønsted acidity was calculated on the basis of area under the peak at ca. 1446 cm^{-1} and 1550 cm^{-1}, respectively (Table 2). Apparently, amount of Lewis acidity sites increased remarkably of 70%, without formation of any Brønsted acid sites after impregnation of vanadium on ST. The finding contradicts with an earlier report which claimed a decrease in Lewis acidity and an increase in Brønsted acidity when vanadia was supported on a metal oxide support (Datka *et al*., 1992). The discrepancy could be due to different sources and material preparation methods applied. In the present study, tetrahedral vanadium probably reacted with hydrated tetrahedral titanium species or directly with Si-O-Si on the aerogel, leading to creation of more Lewis acidic sites in sample V/ST. Consequently, more isolated titanium species were detected in the sample (see Figure 2).

The proposed structure of Lewis acid sites in sample V/ST is shown in Figure 5b. Additional peaks at 1640 cm^{-1} and 1550 cm^{-1} attributed to adsorbed pyridine bound corresponding to Brønsted acid sites were found in sample SO$_4$_V/ST. Like SO$_4$/ST, SO$_4$_V/ST possesses both Lewis and Brønsted acid sites. It is noteworthy that the amount of both Lewis and Brønsted acid sites in SO$_4$_V/ST are slightly higher than those of SO$_4$/ST (Table 2). Since electro negativity of vanadium (1.63) is higher than that of titanium (1.54), it is believed that more Brønsted acidity was available with formation of V(OSi)$_2$OH-O-SO$_3^-$ (Figure 5c) in which two protons could be easily released. In our recent work, it has been demonstrated that interaction between vanadium and phosphate was crucial for Brønsted acidity generation in silica-titania aerogel, leading to high yield of diol (Lee *et al*., 2009).

Table 2: Amount of acid sites calculated from Pyridine-FTIR data of ST and sulfate-vanadium modified ST catalysts at 150°C

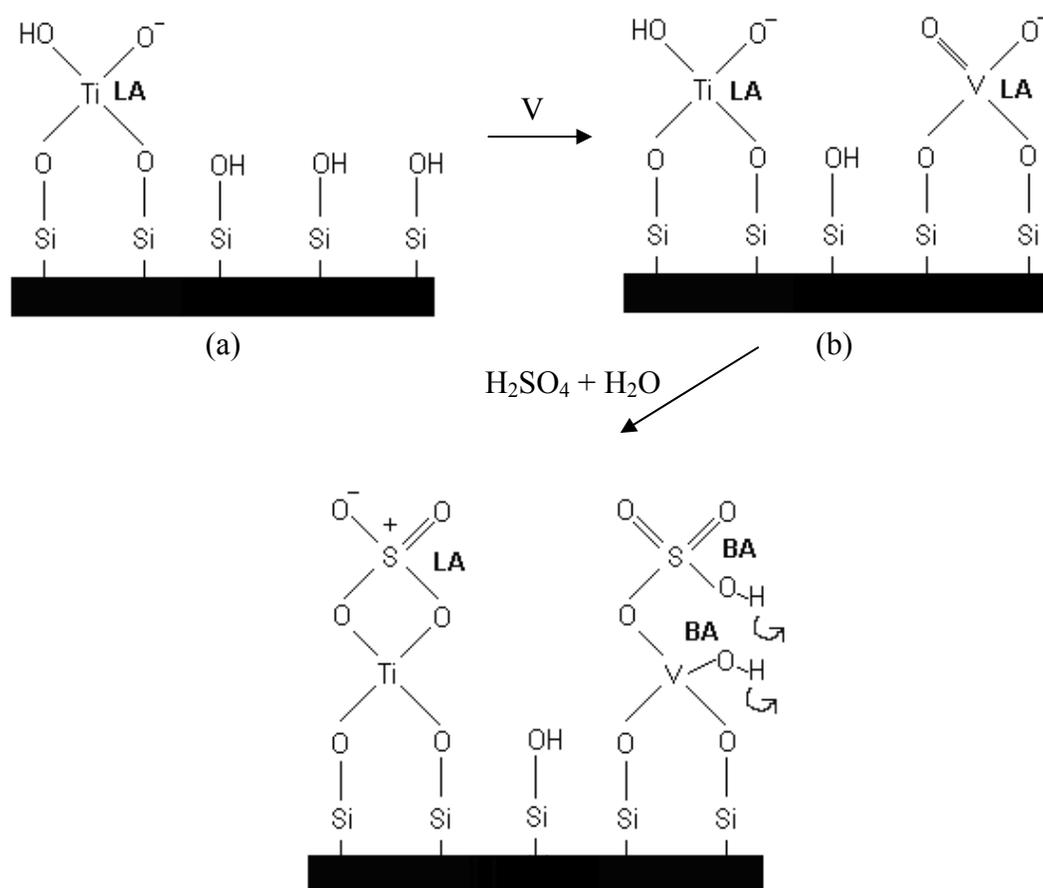| Catalyst	Lewis acid (μmol pyridine g^{-1})	Brønsted acid (μmol pyridine g^{-1})
ST	9.7	0
SO$_4$/ST	11.6	4.5
V/ST	16.6	0
SO$_4$_V/ST	11.7	5.1

Figure 5: Proposed model of (a) ST; (b) V/ST; and (c) SO$_4$_V/ST showing the formation of Lewis acid (LA) and Brønsted acid (BA) sites.

(iv) Catalytic Activity

A catalytic epoxidation of 1-octene at 70°C was carried out for the catalytic performance of the synthesized samples. Table 3 shows the yield of 1,2-epoxyoctane and 1,2-octanediol over ST and sulfate-vanadium modified ST catalysts. The catalyst activity in the epoxidation of 1-octene of all modified ST samples was significantly improved in comparison with the parent material, ST. Evidently, sulfated silica-titania aerogel (SO$_4$/ST) appears to be the best candidate in producing 1,2-epoxyoctane, followed by SO$_4$_V/ST, V/ST and ST. The sulfate treatment has facilitated formation of tripodal titanium species which is

recognized as more active oxidative site compared to dipodal and tetrapodal titanium species (Wang *et al.,* 2004). This explains the excellent catalytic activity of SO_4/ST and SO_4_V/ST in epoxidation (Ling *et al*., 2008). The poorer performance of SO_4_V/ST could be attributed to tendency of combination of sulfate and vanadium in silica-titania aerogel to convert Ti species into not only hydrated tetrahedral Ti, but also into isolated tetrahedral Ti and octahedrally coordinated Ti species that are less active in epoxidation. Meanwhile, the improved catalytic behavior of V/ST as compared to ST is due to formation of some hydrated tetrahedral Ti species in V/ST (Figure 2). Besides, it is believed that V^{5+}=O at surface could act as oxidative site in epoxidation (Dőbler *et al*., 2002).

Table 3: Catalytic performance of ST and sulfate-vanadium modified ST samples on transformation of 1-octene to 1,2-octanediol at 70°C for 24 h.

Catalyst	Yield of 1,2-epoxyoctane (μmol)	Yield of 1,2-octanediol (μmol)
ST	13 ± 1.0	0
SO_4/ST	189 ± 10.5	327 ± 15.7
V/ST	88.7 ± 4.3	212 ± 3.8
SO_4_V/ST	123 ± 3.4	127 ± 5.2

Theoretically, more diols can be produced using a catalyst of superior Brønsted acidity since the formation of diols from epoxides is catalyzed by Brønsted acidic site. However, different finding was observed in the present study. Although SO_4_V/ST has higher surface area and larger amount of Brønsted acid sites as compared to SO_4/ST, SO_4_V/ST produced lesser diols. The reasonable explanation for this phenomenon could be the weaker oxidative sites in SO_4_V/ST as compared to SO_4/ST. A stronger oxidative site plays a key role in producing epoxides which are needed to generate high amount of diol in a consecutive reaction. Apart from that, it is believed that some sulfate groups have reacted with vanadia during the wet impregnation process, bringing to creation of vanadium sulfate ($VOSO_4$) on the surface of silica-titania aerogel. The $VOSO_4$ formed may have retarded the catalytic activity of SO_4_V/ST by hindering the reaction between catalyst and reactant.

It has been reported that titanium silicalite (TS-1) loaded with 20 wt% sulfated zirconia (20SZ/TS-1) was a potential bifunctional catalyst in which the tetrahedral coordinated Ti in TS-1 acted as oxidative sites while sulfated zirconia deposited on the surface of TS-1 played a role as Brønsted acid sites (Prasetyoko *et al.*, 2005b). Its catalytic activity of in producing 1,2-epoxyoctane is much better (3 times higher in yield) than that of SO$_4$/ST. This material, however, produced only 28 μmol 1,2-octanediol in a similar reaction after 24 hours. The poor catalytic performance of 20SZ/TS-1 in the consecutive transformation to form diols could be due to its relatively small pore size and insufficient amount of Brønsted acidic sites.

On the other hand, V/ST showed remarkable activity toward the formation of 1,2-octanediol. However, from the pyridine adsorption studies, no significant Brønsted acid sites were observed on V/ST. It is suggested that the Brønsted acid sites might not have generated from the V/ST catalyst itself, but rather formed during the reaction in the presence of water from the reaction mixtures. Its catalytic mechanism as a bifunctional catalyst is currently under investigation.

Conclusions

An increment of Brønsted acidity of 5.1 μmol pyridine g^{-1} was observed in sulfate-vanadium treated silica-titania aerogel. This catalyst possesses high surface area of 462 m^2/g. Besides, both titanium tetrahedrally coordinated and vanadium acted as oxidative sites in the catalyst. However, loading of both vanadium and sulfate on silica-titania aerogel may have led to generation of weaker oxidative sites.

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