Synthesis and Characterization of Acid Modified Silica-Titania Aerogel as Oxidative-Acidic Bifunctional Catalyst

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Abstract—Acid treatment using H_2SO_4, HCl and H_3PO_4 has been carried out in an attempt to improve catalytic performance of silica-titania aerogel. X-ray diffraction results showed the amorphous structure of the aerogels remained after the acid impregnation and calcinations steps. Hammert analysis revealed these acid modified silica-titania aerogels were superacids with pKa < -14.52. Different Ti species was observed in the samples upon the acid treatment. As compared to silica-titania aerogel, Lewis acidity increased remarkably in HCl treated sample without formation of any Brønsted acid site. Meanwhile, H_2SO_4 and H_3PO_4 treated samples possessed both Lewis and Brønsted acid sites. The catalytic performance of these samples was evaluated through a consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane using aqueous hydrogen peroxide as oxidant.

Index Terms—Bifunctional catalyst, Brønsted acidity, oxidative site, silica-titania aerogel.

I. Introduction

Considerable efforts have been made for developing a bifunctional catalyst which is potentially active for a consecutive process. Existence of two different active sites in the material makes it a promising catalyst in production of diols that currently are produced industrially via a two-step sequence. A bifunctional catalyst of sulfated zirconia TS-1 possesses both oxidative site and Brønsted acidity [1]. Tetrahedrally coordinated Ti species in the framework of silicalite was an efficient oxidative site for epoxidation. However, limited acidity from octahedral zirconia containing sulfate has restricted the production of diols.

Since last decade, silica aerogel has been widely used as a catalyst support as it has extremely large specific surface areas and high porosities. Silica-titania aerogel is a promising catalyst for epoxidation due to the highly distribution of Ti^{4+} species in the catalyst [2]-[4]. Unfortunately, these materials including silica-titania aerogels do not consists of Brønsted acidity, but only Lewis acidity [5]. Thus, there was no transformation of diols from epoxides by using these materials, because presence of Brønsted acidity is crucial for the conversion.

Modification via acid treatment is one of the approaches used to enhance the Brønsted acidity in a catalyst. Generation of Brønsted acidity in sulfated Al-MCM-41 and phosphate-impregnated MCM-41 have been reported [6], [7]. Nevertheless, no any oxidative site was detected in these MCM-41 based materials. In our recent study, it has been demonstrated that sulfated silica-titania aerogel was an excellent oxidative-acidic bifunctional catalyst in a consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane [8]. In this present work, we have undertaken to study the effect of different acids on the properties and catalytic activity of silica-titania aerogel. Results were compared with that of sulfated silica-titania aerogel.

II. Experimental

A. Synthesis of Acid Treated Silica-Titania Aerogel

Silica-titania aerogel (ST, molar ratio of Si:Ti = 33:1) was prepared through sol-gel direct synthesis and high temperature supercritical process as described elsewhere [8]. Rice husk ash and titanium tetrachloride (Fluka, >98%) were used as precursors of Si and Ti, respectively. A mixture of rice husk ash, NaOH and H_2O was stirred at 90°C for 2 days. Then, the mixture was filtered to get sodium silicate solution. $TiCl_4$ was introduced into the solution before gelation process which was activated by adding sufficient amount of concentrated H_2SO_4 (98%) to the solution. After 2 days aging at room temperature, the gel formed was neutralized with distilled water. The Soxhlet extraction was carried out and finally the aerogel was produced by supercritically drying the alcogel from N_2.

Acid modified silica-titania materials were prepared by impregnation method as follow: 2 g of ST was added into 25 mL of 0.2 M acid solution. The mixture was stirred vigorously at room temperature for 2 h before drying at 100°C for 2 days. The obtained dry gel powder was ground and followed by calcination at 500 °C for 7 h. The resultant samples were labeled follow the acid treatment, e.g. silica-titania aerogel modified with HCl was given notation as ST_HCl.

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B. Characterization

The surface area and pore volume of the samples was determined by means of BET N_2 adsorption using Qsurf (M series) surface area analyzer. Meanwhile, the crystallinity of the samples was identified by X-ray diffraction (XRD), using a Bruker Advance D8 using Siemens 5000 diffractometer with the Cu K_α (λ = 1.5405 Å) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. XRD analysis was carried out at a step of 0.02^o and step time 1 s over 2θ range of 2° to 50°. Fourier Transmittance Infrared (FTIR) measurements were performed on a Shimadzu Fourier Transform Infrared (FTIR) spectrometer, with a spectral resolution of 2 cm^{-1}, scans 10 s by KBr pellet method. UV-Vis diffuse reflectance spectra were collected under ambient conditions using a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer over the range from 190 to 800 nm.

For acidity evaluation, about 14 mg of the sample was pressed to obtain a 13 mm disk. The sample was introduced in the infrared cell with CaF$_2$ windows. The sample was heated at 200 ^{o}C in vacuum condition for 3 h. The infrared spectra were recorded at room temperature using Shimadzu 2000 FTIR spectrometer at 2 cm^{-1} resolution. The types of acid sites were determined using pyridine as a probe molecule. Pyridine was absorbed at room temperature for a minute, continued by desorption at 150°C for an hour. Acid strength of the samples was determined by the Hammert indicator method. Sufficient amount of sample was heated at 473 K for 2 h in order to remove water, before it contacted to the Hammert indicator in dried cyclohexane.

C. Catalytic Testing

The catalytic activity of the prepared materials was tested in epoxidation of 1-octene using aqueous H_2O_2 as oxidant. The reaction mixture containing 8 mmol of 1-octene (Fluka, 97%), 15 mmol of H_2O_2 in H_2O (Hanns, 35%), 10 mL of acetonitrile (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. The sample (0.050 g) was then added to the solution. The reaction was carried out in an oil bath under stirring at 70 ^{o}C for 24 h. The products of the reaction were analyzed using GC-and GC-MS. Three set of experiments were carried out for each catalyst.

III. RESULTS AND DISCUSIONS

A. Physical Properties

ST was semi transparent and light fluffy powder. All the acid treated ST materials were in white even after the 500 ^{o}C calcination step in air. A slight loss in surface areas was realized with addition of HCl and H_2SO_4 (Table 1). This could be attributed to a coalescence process in the presence of acid during calcinations. Besides, 90% loss in surface area and pore volume was observed in phosphated sample, strongly suggesting the destruction of aerogel structure.

The increase of pore volume of HCl modified ST aerogel was due to the partial breakage of pore structure of aerogel. The presence of Cl$^-$ ions during the impregnation might also change the ionic strength of the gel, leading to the formation of bigger pores and lower surface area.

TABLE 1. SURFACE AREA AND PORE VOLUME OF ST AND ACID MODIFIED ST SAMPLES.

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)
ST	550	0.98
ST_HCl	427	1.05
ST_H$_3$PO$_4$	44	0.11
ST_H$_2$SO$_4$	384	0.96

The amorphous structure of the aerogels was remained after the acid treatment and calcinations steps (Fig. 1). No peaks corresponding to either the Ti or acid was observed on the XRD diffractograms, indicating that acid was highly dispersed on the surface of silica-titania aerogel, or were incorporated into the aerogel framework. The phenomena could be explained by Ti species that present neither in anatase nor rutile phase.
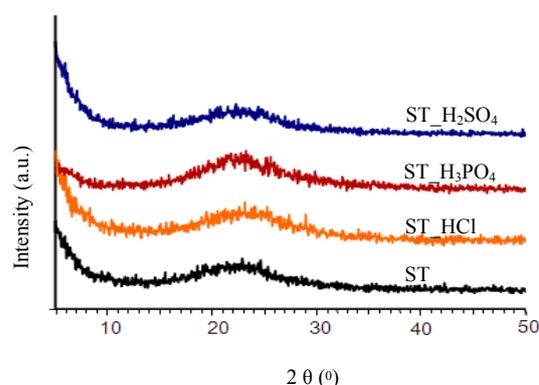
Fig. 1. XRD diffractograms of ST and acid modified ST samples

Fig. 2 shows the UV-Vis DR spectra of ST and acid-modified ST samples. Generally, three absorption bands at 210, 250 and 296 nm were observed in these samples. The weak absorption band at 210 nm was corresponded to isolated, tetrahedrally coordinated Ti species. This electronic transition was assigned to a $O^{2-} \rightarrow Ti^{4+}$ charge transfer transition of tetrahedrally coordination Ti. The absorption band at 250 nm was associated with hydrated, tetrahedrally coordinated Ti species. Like ST_H$_2$SO$_4$, a high intense band at 250 nm was observed in ST_H$_3$PO$_4$. This could be explained by the more hydrophilic character of the H_3PO_4 modified sample, facilitating the hydration of Ti. Although the morphology of aerogel is amorphous in the long range, obviously the Ti species in both H_2SO_4 and H_3PO_4 modified silica-titania aerogels are linked to a continuous chain of tetrahedrally coordinated silicate polymer. On the other hand, the band at 296 nm was due to the octahedrally coordinated or polymetric Ti species. Apparently, the results show that the impregnation of HCl into ST brought in formation of more octahedrally coordinated Ti species in ST_HCl. Therefore, we could conclude that the type of acid used in the impregnation process did affect the Ti species formed.

The FTIR spectra of ST and acid-modified ST samples show the typical silicate absorptions at about 1100 cm^{-1} and 470 cm^{-1}, which could be attributed to Si-O-Si bending and stretching vibrations (Fig. 3). The band at 800 cm^{-1} was associated with symmetric Si-O-Si stretching. The absorption

at 963 cm^{-1} was due to surface Si-OH vibrations and possibly overlaps absorptions of Si-O-Ti bond, which was also corresponded to tetrahedral Ti. The shift of the bands at 800 cm^{-1} and 963 cm^{-1} to higher wavenumber was observed in ST_H$_2$SO$_4$ and ST_HCl. This indicates that the impregnation of acid into ST has weakened the Si-O-Ti and Si-O-Si bonding, bringing to a longer bond length and hence decreasing the force constant of the bonds in these samples. Meanwhile, the band at ~970 cm^{-1} appeared to be diminished in H$_3$PO$_4$ treated ST, only a weak shoulder was observed at ~1000 cm^{-1}. This may suggest that the Si-O-Si bonding in silica-titania aerogel decreased dramatically after treatment with H$_3$PO$_4$. This observation well agreed with the significant loss in surface area in this sample.
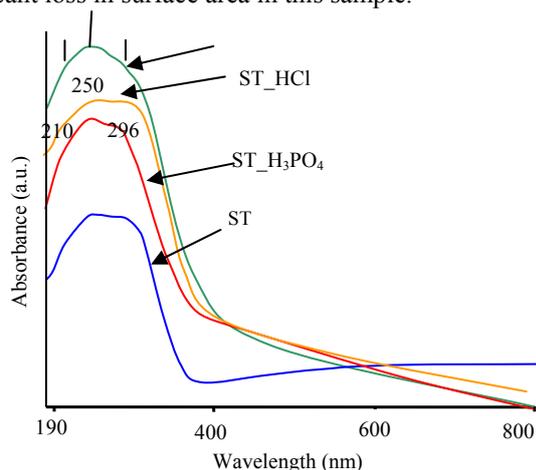
Fig. 2. UV-Vis diffuse reflectance spectra of ST and acid modified ST samples
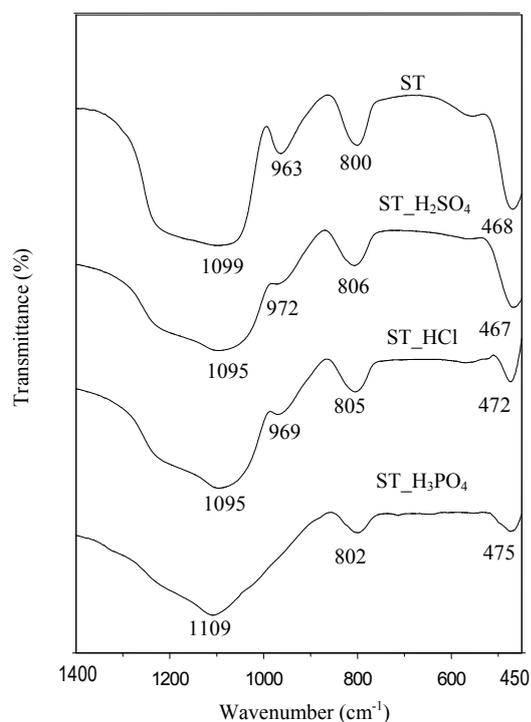
Fig. 3. FTIR spectra of ST and acid modified ST samples

B. Acidity

Fig. 4 shows the FTIR spectra of the ST and acid treated ST samples after evaluation at 300 ^{o}C for 3 h under vacuum. In the region of hydroxyl group, the peak at ~3733 cm^{-1}, which is assigned as silanol hydroxyl groups, can be clearly observed for ST, ST_H$_2$SO$_4$ and ST_HCl. However, this band was diminished in ST_H$_3$PO$_4$, suggesting that the phosphate groups are located in the space or sites previously occupied by silanols groups. It is also possible that phosphate groups reacted with Si-OH groups and hence led to enhancement of Brønsted acidity sites. The latter explanation coincides with the observation in FTIR analysis (Fig. 3), which shows the dramatically decrease of Si-OH bonding in ST_H$_3$PO$_4$.

The acidity of the ST and acid treated ST samples was monitored by FTIR using pyridine as a probe molecule. Fig. 5 shows that the infrared spectra of the samples in the pyridine region. The spectra of ST, ST_ and ST_HCl showed the adsorption bands at ~1600 cm^{-1} and ~1446 cm^{-1} which are associated to pyridine interacting with Lewis acid sites. Meanwhile, the additional peaks at ~1638 cm^{-1} and ~1548 cm^{-1} in the spectra of ST_H$_2$SO$_4$ and ST_H$_3$PO$_4$ are attributed to adsorbed pyridine bound coordinatively with Brønsted acid sites. Table 3 lists the amount of acid sites calculated from pyridine-FTIR of all the samples at 150°C.
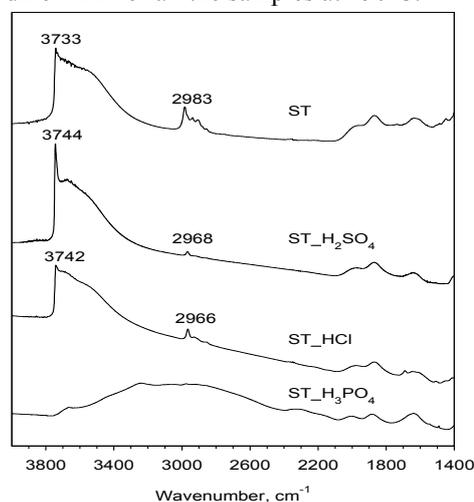
Fig. 4. The pyridine –FTIR spectra of ST and acid-treated ST Samples after evacuation at 300°C for 3 h in vacuum
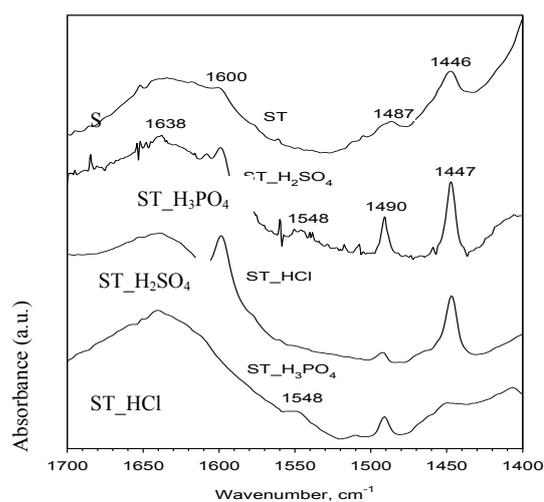
Fig. 5. The pyridine –FTIR spectra of ST and acid-treated ST samples after pyridine adsorption and evacuation at 150 ^{o}C for 1 h

The acidity study revealed that: (1) ST does not possess Brønsted acidity, but only Lewis acidity, which well agrees with the previous report [5]; (2) Lewis acidity sites increased slightly after treatment with H2SO4 and HCl, but the presence of Lewis acid sites in ST_H3PO4 is negligible; (3)

Brønsted acid sites presented only in H2SO4 and H3PO4 treated ST samples.

TABLE 3. AMOUNT OF ACID SITES CALCULATED FROM PYRIDINE-FTIR DATA OF ST AND ACID MODIFIED ST SAMPLES AT 150 oC.

Sample	Lewis acid (μmol pyridine g^{-1})	Brønsted acid (μmol pyridine g^{-1})
ST	9.7	0
ST_HCl	10.2	0
ST_H_3PO_4	0	0.7
ST_H_2SO_4	11.6	4.5

The proposed structure of the samples showing possible Lewis and Brønsted acid sites is shown in Fig. 6. In fact, partial conversion of hydrated silica-titania aerogel surface by HCl would form a surface that contains both Cl⁻ and OH⁻. Since Cl⁻ is more electronegative than OH⁻, the Lewis acidity of ST_HCl is increased. The intensity of silanol groups appeared to be reduced after HCl treatment (Fig. 3). Similar finding was reported on HCl treated activated alumina [9]. Alternatively, HCl could have reacted with TiO^{2+} in non-framework, subsequently contributed to formation of $TiCl_4$ and led to increase of Lewis acid sites in ST_HCl. Process of detitanation occurred during the acid treatment may help in creation of more Lewis acid sites in this sample. On the other hand, attack of phosphate groups to Lewis acid sites in silica-titania aerogel is expected in ST_H_3PO_4. Thus, presence of Brønsted acid sites is dominant in H_3PO_4 treated ST sample.
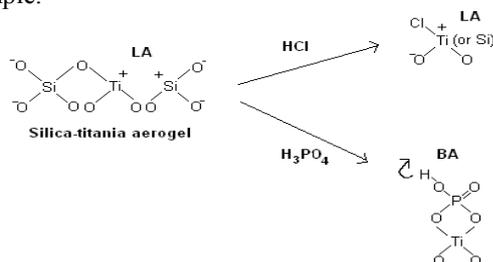
Fig. 6. Scheme proposed for silica-titania aerogel (ST) and acid-treated ST showing possible acid sites (LA – Lewis acid sites and BA - Brønsted acid sites)

Hammert indication analysis revealed that ST is only able to change the basic forms (colourless) of chalcone (pKa = -5.6) and anthraquinone (pKa = -8.2) to yellow colour, indicating that its acidity is in the range of $-11.35 < H_o < -8.2$. However, ST_HCl and ST_H_3PO_4 give an outstanding result where these acid treated ST samples turned the basic forms of 2,4- dinitroflourobenzene (pKa = -14.52). Thus, the acid strength of these samples is estimated to be $H_o < -14.52$. This implies that acid strength of silica-titania aerogel has been increased dramatically through acid treatment. Since acids stronger than $H_o = -12$ are superacids, both ST_HCl and ST_H_3PO_4 are superacids.

C. Catalytic Activity

The catalytic activity of the ST and acid-treated ST was evaluated in the epoxidation of 1-octene with aqueous H_2O_2 in acetonitrile at 70 °C for 24 h. As shown in Table 2, ST showed no noticeable activity toward the formation of 1,2-epoxyoctane and consequently, there was no 1,2-octanediol produced from the reaction. Among the catalysts used, ST_H_2SO_4 showed remarkable higher activity (more than fourteen times higher in yield for 1,2-epoxyoctane) compared to ST. This phenomenon was explained by the presence of tripodal Ti active site [*i.e.* $Ti(OSi)_2(SO_3)OH$] that is the most active hydrated, tetrahedrally coordinated Ti species in sulfated materials [8, 10]. Besides, ST_H_2SO_4 sample appears to be the only efficient catalyst in producing 1,2-octanediol, indicating the presence of sufficient amount of Brønsted acid sites in the sample as was reflected in pyridine adsorption analysis .

On the other hand, a slight increase of 1,2-epoxyoctane produced was observed by using ST_HCl as catalyst. It may imply that the more hydrated, tetrahedrally coordinated Ti species was formed during HCl treatment as compare to untreated ST since the Ti(IV) species could be the real active species in the epoxidation reaction. Besides, trace of diol was found in the end of reaction, even though no Brønsted acidity was detected in ST_HCl sample. It is suggested that the Brønsted acid sites were not generated from the ST_HCl catalyst itself, but were rather formed during the reaction in the presence of water from the reaction mixtures.

No improvement in catalytic activity was observed in H_3PO_4 modified sample. Although amount of hydrated, tetradhedrally coordinated Ti species increased upon H_3PO_4 treatment as shown in UV-Vis DR analysis, the destruction of aerogel structure may have restricted the reaction at the active sites. Higher porosity with larger pore volume is required for transformation of 1-octene to epoxide and subsequently to diols which are considerably large molecules. Alternatively, formation of the less active tetrahedrally coordinated Ti species that are bipodal and tetrapodal closed lattice sites was favored in H_3PO_4 treatment. Even though Brønsted acid sites also detected in ST_H_3PO_4, no 1,2-octanediol formed after the reaction. This indicates that 1,2-octanediol can only be produced after formation of sufficient amount of 1,2-epoxyoctane.

TABLE 2. CATALYTIC PERFORMANCE OF ST AND ACID MODIFIED ST SAMPLES

Catalyst	1,2-epoxyoctane (μmol)	1,2-octanediol (μmol)
ST	13 ± 1.0	0.0
ST_HCl	24 ± 2.3	8 ± 0.7
ST_H_3PO_4	9 ± 1.2	0.0
ST_H_2SO_4	189 ± 10.5	327 ± 15.7

IV. CONCLUSION

Effect of acid treatment on silica-titania aerogel as a bifunctional catalyst was explored. Aerogel structure was remained after acid modification using HCl and H_2SO_4, while destruction of aerogel structure was observed in H_3PO_4 treated sample. Hydrated, tetrahedrally coordinated Ti species appeared dominantly in both H_3PO_4 and H_2SO_4 treated samples. Besides, Brønsted acid sites were only detected in H_3PO_4 and H_2SO_4 treated samples; while increment of Lewis acidity was found in HCl treated sample without formation of Brønsted acid sites. It had been demonstrated that ST_H_2SO_4 is a promising bifunctional oxidative and acidic catalyst. Slight improvement in catalytic activity was shown in HCl treated sample. However, H_3PO_4 treated sample was inactive in consecutive transformation of 1-octene to 1,2-octanediol through formation of 1,2-epoxtoctane using aqueous H_2O_2.

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