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Abstract

Titanosilicalite (TS-1) has been successfully modified by sulfation to exhibit enhanced catalytic activity in the oxidation of 1-octene with aqueous H₂O₂. A high activity of the sulfated TS-1 was related to modifications of the local environment of Ti active site upon interaction with the SO₄²⁻.

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1. Introduction

The discovery of the framework substituted microporous materials titanium silicalite-1 (TS-1) was one of the most important developments in heterogeneous catalysis with in the last decade [1]. These materials exhibit extremely high selectivity in oxidation reactions using hydrogen peroxide, with water as the major byproduct. Since there is a low concentration of Ti present in TS-1 the catalytically active Ti centers are believed to be site isolated from each other. This site isolation is thought to give rise to its unique catalytic activity and selectivity. It has been reported that the catalytic activity of TS-1 for olefin epoxidation with aqueous H₂O₂ could be enhanced by trimethylsilylation in order to produce hydrophobic TS-1 [2]. However, trimethylsilyl group can block the pore of the TS-1 since its size is considerably big. Here, we demonstrated a simple method to enhance the catalytic activity of TS-1 in

epoxidation of 1-octene with aqueous H₂O₂ by sulfation. This simple method can eliminate the possibility of pore blockage.

2. Experimental

2.1. Synthesis

TS-1 (2% of Titanium, mol%) was prepared according to a procedure described earlier [1,3], using reagents, i.e., tetraethyl orthosilicates (Merck, 98%), tetraethyl orthotitanate (Merck, 95%) in isopropyl alcohol, tetrapropylammonium hydroxide (Merck, 20% TPAOH in water) and distilled water. The hydrothermal crystallization was carried out at 175 °C under static condition in the stainless steel autoclave for 4 days.

Sulfated TS-1 was prepared by impregnation method as follows: About 1 g of TS-1 was added into 25 ml of H₂SO₄ 0.5 M under vigorous stirring at 80 °C for 3 h. After evaporation of water, the solid was dried at 100 °C for 24 h. The solid sample was then calcined at 550 °C for 3 h. The sample was denoted as SO₄/TS-1.

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2.2. Characterizations

The solid structure was determined by using X-ray diffraction (XRD), infrared (IR) and UV–Vis Diffuse Reflectance (UV–Vis DR) spectroscopy techniques. All samples were characterized by powder XRD for the crystallinity and phase content of the solid materials using a Bruker Advance D8 Diffractometer with the Cu K α ($\lambda = 1.5405 \text{ \AA}$) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. The sample was scanned in the 2θ range between 5° and 50° . IR spectra of the samples were collected on a Perkin–Elmer Fourier Transform Infrared, with a spectral resolution of 2 cm^{-1} , scans 10 s, at room temperature by KBr pellet method. The framework spectra were recorded in the region of $1400\text{--}400 \text{ cm}^{-1}$. UV–Vis DR spectra were recorded under ambient conditions on a Perkin–Elmer Lambda 900 UV/Vis/NIR spectrometer. The acidity of the solids characterized by absorbed base probe molecule. The wafer of the sample (10–12 mg) was locked in the cell equipped with CaF_2 windows, and evacuated at 400°C under vacuum condition for 4 h. Pyridine as probe molecule was introduced into the evacuated sample at room temperature. IR spectra of the sample was monitored at room temperature after desorption of pyridine at 150°C for 1 h.

2.3. Epoxidation of 1-octene

All reactions were carried out at room temperature with 1-octene (1.0 ml), 30% H_2O_2 (0.5 ml), a mixture of methanol (5 ml) and acetone (5 ml) as solvent, and catalyst (50 mg) with stirring. The products of reaction were analyzed by GC and GC–MS.

3. Results and discussion

XRD was used to characterize the structure and the crystallinity of the TS-1 and $\text{SO}_4/\text{TS-1}$. All samples show similar XRD patterns characteristic of MFI structure type of zeolite. Introduction of SO_4^{2-} anions into the TS-1 has no effect on the sample crystallinity, with less than 1% changes. This suggests that the MFI structure of TS-1 is still maintained after the introduction of SO_4^{2-} . IR spectra of TS-1 and $\text{SO}_4/\text{TS-1}$ samples show a peak at around 970 cm^{-1} which is a characteristic for titanium with tetrahedral structure (Fig. 1). This band appears to be diminished in the sulfated material, suggesting the decrease in the amount of tetrahedral titanium in $\text{SO}_4/\text{TS-1}$. IR spectrum of $\text{SO}_4/\text{TS-1}$ shows a new peak at around 1384 cm^{-1} which is corresponded to the asymmetric stretching vibration of the covalent S=O for SO_4^{2-} ion.

Fig. 2 shows UV–Vis DR spectra of TS-1 and $\text{SO}_4/\text{TS-1}$. The band in the range of 190–220 nm is attributed

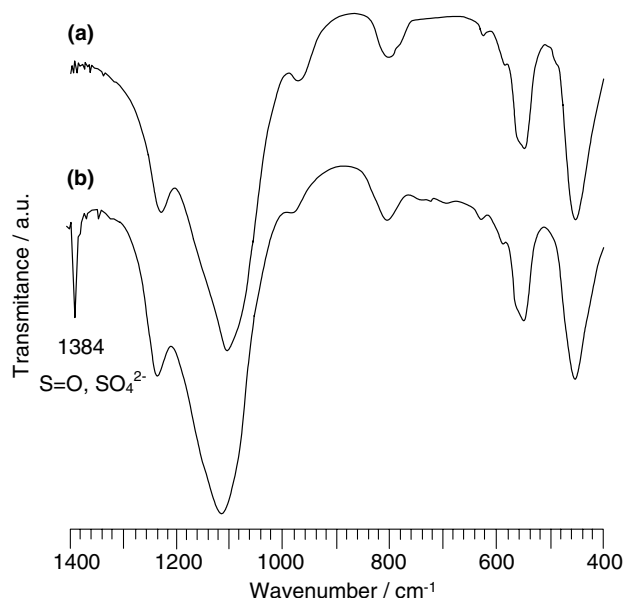


Fig. 1. FTIR spectra of: (a) TS-1; (b) $\text{SO}_4/\text{TS-1}$.

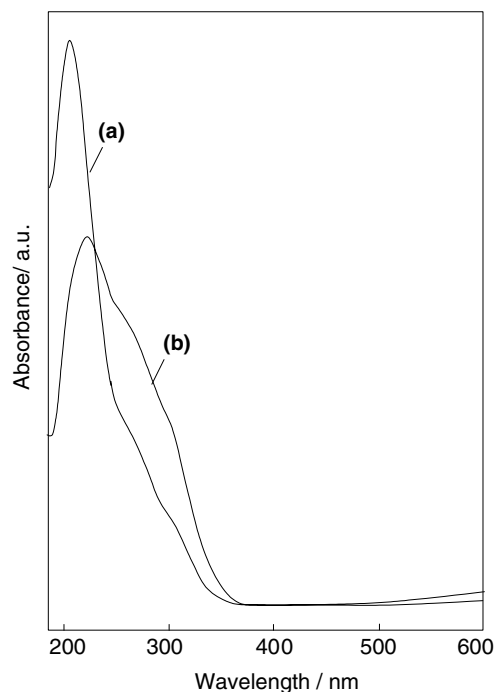
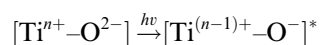


Fig. 2. Absorption spectrum of: (a) TS-1; (b) $\text{SO}_4/\text{TS-1}$.

to a charge-transfer of the tetrahedral titanium sites between O^{2-} and the central Ti(IV) atoms, while octahedral Ti is observed at around 310–330 nm [4,5]. It shows that, for TS-1, only single high intense band at around 208 nm can be observed. This band is attributable to titanium in the tetrahedral structure. Impregnation of SO_4^{2-} into the TS-1 shows a medium intense band at around 215–228 nm and a shoulder band at around 270–312 nm, characteristic for titanium with tet-

rahedral and octahedral structure, respectively. The peak intensity of tetrahedral titanium for $\text{SO}_4/\text{TS-1}$ is lower than that of the parent sample (TS-1). The decrease in intensity of the tetrahedral titanium and the formation of the octahedral titanium indicate the occurrence of the transformation of some of the tetrahedral titanium framework to the octahedral structure or the extraframework during the sulfation. It has been calculated that 49% of tetrahedral titanium in the parent sample have been modified by sulfation.

As shown in Fig. 2, the wavelength of absorption band of the tetrahedral titanium sites (i.e., 288 nm) of $\text{SO}_4/\text{TS-1}$ is higher than that of TS-1 (i.e., 208 nm). It could be that the Ti–O–S bonding in $\text{SO}_4/\text{TS-1}$ lowered the charge-transfer excited state involving an electron transfer from O^{2-} to Ti^{n+} [6]:



This phenomenon is supported by the fact that the band at 970 cm^{-1} of TS-1, which is corresponded to tetrahedral titanium, is shifted to higher wavenumber in $\text{SO}_4/\text{TS-1}$ (see Fig. 1). The shift to higher wavenumber is expected since the presence of SO_4^{2-} species in $\text{SO}_4/\text{TS-1}$ weakened the Ti–O–Si bonding, resulting in a longer bond length and hence decreasing the force constant of Ti–O–Si.

The acidity of the samples was characterized by pyridine adsorption. TS-1 and $\text{SO}_4/\text{TS-1}$ only show the peak at around 1450 cm^{-1} (which is corresponded to Lewis acid site), while the peak at around 1545 cm^{-1} (which is corresponded to Brönsted acid site) was not observed (Fig. 3). This indicates that all samples only contain Lewis acid sites. It has been calculated that the amount of the Lewis acid sites in TS-1 and $\text{SO}_4/\text{TS-1}$ were 12 and $8\text{ }\mu\text{mol g}^{-1}$, respectively, indicating a decrease of 33% in the Lewis acid concentration of $\text{SO}_4/\text{TS-1}$ from the TS-1. This result suggests that the removal of tetrahedral titanium from the lattice to form octahedral species

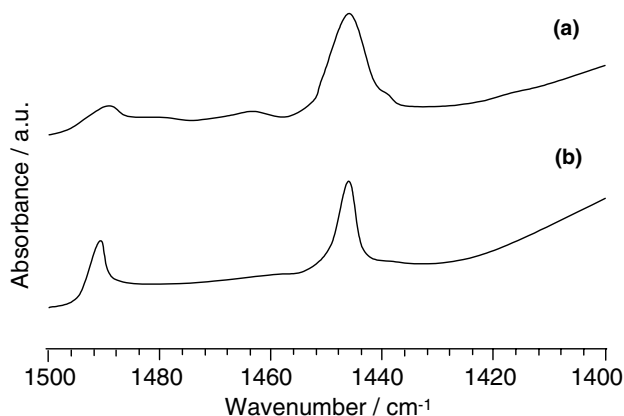


Fig. 3. FTIR spectra of: (a) TS-1; (b) $\text{SO}_4/\text{TS-1}$ after following treatments: heated at $400\text{ }^\circ\text{C}$ for 4 h in vacuum, adsorbed pyridine at room temperature, and desorbed pyridine at $150\text{ }^\circ\text{C}$ for 1 h.

is the reason for the decrease in the acidity, since the amount of the Lewis acid sites correlate to the amount of tetrahedral titanium. No diol is observed in the reaction product of the epoxidation of 1-octene with aqueous H_2O_2 confirming that no Brönsted acid sites are present in the samples.

The infrared spectra of the TS-1 and $\text{SO}_4/\text{TS-1}$ in the range of hydroxyl stretching regions at $4000\text{--}3000\text{ cm}^{-1}$ were recorded after evacuation in vacuum at $400\text{ }^\circ\text{C}$ for 4 h (Fig. 4). TS-1 shows an intense band at 3736 cm^{-1} and a broad band at 3526 cm^{-1} , characteristics for terminal silanol hydroxyl groups and hydroxyl groups with hydrogen bonding of water molecule with silanol groups, respectively [5]. The sulfation of TS-1 caused the sharp band of silanol groups to decrease significantly and becomes broader in the ranges of $3740\text{--}3726\text{ cm}^{-1}$, suggesting the formation of defect sites in the surface of TS-1. Meanwhile, the broad band for hydroxyl groups around 3500 cm^{-1} increases due to the hydroxyl groups are bounded on the sulfur centers.

As shown in Fig. 5, sulfation onto the surface of TS-1 increases its epoxidation activity. This phenomenon may be explained in terms of the local environment of Ti active site. It is generally accepted that isolated Ti(IV) are considered the most active species in epoxidation reaction. It has been found that tripodal open lattice site

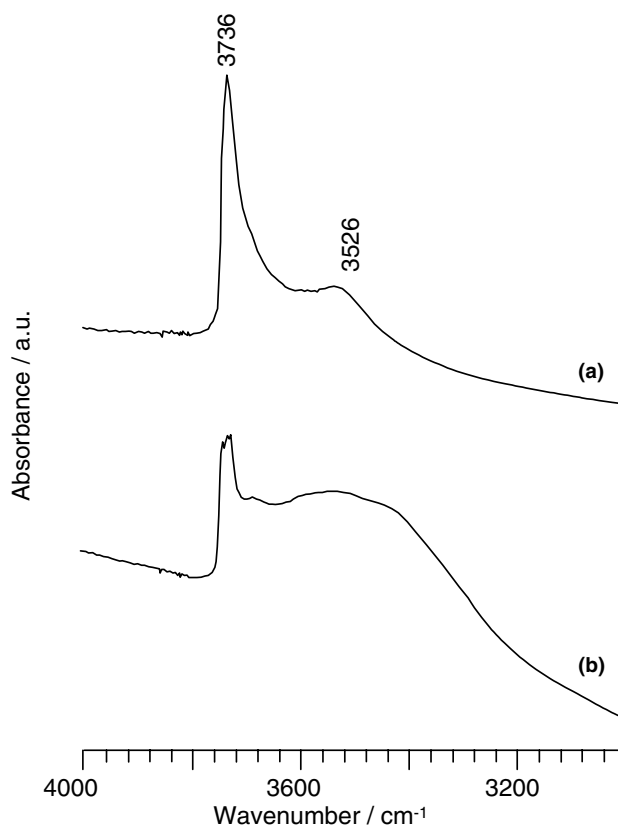


Fig. 4. FTIR spectra of: (a) TS-1; (b) $\text{SO}_4/\text{TS-1}$ after heated at $400\text{ }^\circ\text{C}$ for 4 h in vacuum.

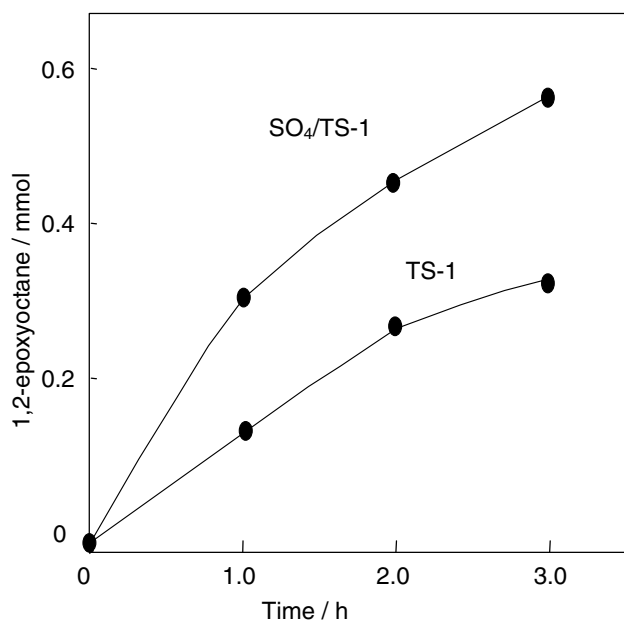


Fig. 5. The yield of 1,2-epoxyoctane on the epoxidation of 1-octene using TS-1 and SO₄/TS-1. The reactions were carried out at room temperature with 1-octene (1.0 ml), 30% H₂O₂ (0.5 ml) and catalyst (50 mg).

[i.e., Ti(OSi)₃OH] of Ti on the TS-1 surface was more active compared to the bipodal [i.e., Ti(OSi)₂(OH)₂] and the tetrapodal closed lattice sites [i.e., Ti(OSi)₄] [7,8]. Based on these findings, the effect of sulfation on increasing the epoxidation activity of SO₄/TS-1 can be explained by the presence of tripodal Ti active site. As shown in Fig. 6, it proposes that the bipodal Ti reacted with SO₄²⁻ giving Ti(SiO)₂SO₄ and followed by the hydration of Ti(SiO)₂SO₄ resulting in the tripodal Ti site [i.e., Ti(OSi)₂(SO₃)OH].

The alternative explanation for the higher activity of SO₄/TS-1 is that the possibility of the formation of new sites generated by sulfation on the surface TS-1. The UV–Vis DR spectra shown in Fig. 2 clearly show that Ti has been removed from the lattice to form octahedral species. It is possible that it can migrate to the external surface. Since 1-octene is a relatively large molecule, one considers that an increase the number of external active sites and access on them could be a cause for the higher activity.

Based on the above considerations, the high activity of SO₄/TS-1 for epoxidation of 1-octene by aqueous

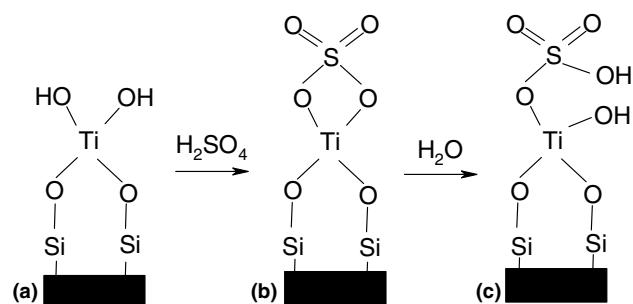


Fig. 6. Proposed model of the local environment structure of Ti: (a) bipodal; (b) tetrapodal; (c) tripodal.

hydrogen peroxide can be considered as the influence of the attachment of SO₄²⁻ to the Ti active sites or alternatively, the formation of new sites generated by sulfation in the surface TS-1.

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