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**ENHANCEMENT OF CATALYTIC ACTIVITY OF
TITANOSILICALITE-1 – SULFATED ZIRCONIA COMBINATION
TOWARDS EPOXIDATION OF 1-OCTENE WITH AQUEOUS
HYDROGEN PEROXIDE**

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Abstract

Titanosilicalite-1 (TS-1) in combination with sulfated zirconia efficiently catalyzes the epoxidation of 1-octene with aqueous hydrogen peroxide. The presence of both octahedral zirconium and sulfate species in the catalysts enhances the epoxidation rates.

Keywords: Titanosilicalite-1, sulfated zirconia, epoxidation

INTRODUCTION

Epoxides are becoming important useful commercial products in the area of petrochemical and fine chemical industries. Many efforts have been made to facilitate the production of epoxides, which include the use of catalysts in the production processes. The breakthrough was achieved by Taramasso in 1983 who reported the preparation and catalytic activity of titanosilicalite-1 (TS-1) [1]. TS-1 represents an important change since it has shown interesting catalytic properties in alkene epoxidations with hydrogen peroxide as the oxidant. Compared to the traditional oxidation reactions, H₂O₂ as the oxidant in all the oxidations catalyzed by TS-1 has the advantage of producing environmentally

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benign water as its by-product. It has been applied to catalytic oxidation of different organic substrates, for example, epoxidation of olefins, hydroxylation of aromatics, amoximation of cyclohexanol and oxidation of alcohols [2,3]. It exhibits an excellent catalytic reactivity and selectivity in different oxidations attributed to coordination of the catalytic oxidation property in titanium and shape selectivity effects in ZSM-5 structure. However, development of the catalysts in order to increase its catalytic activity towards epoxides is still in progress, such as in catalyst preparation and modification [3,4]. Meanwhile, zirconia-silica composite prepared by sol-gel method and zirconia supported on the silica aerosil have been shown to be an active catalyst in the epoxidation of 1-octene using *t*-butyl hydroperoxide (TBHP) as oxidant [5,6]. Its activity is related with the structure of zirconium in the materials, i.e. coordinatively unsaturated configuration. We now demonstrate that the catalytic activity of TS-1 towards the epoxidation of 1-octene with aqueous hydrogen peroxide can be enhanced by deposition of sulfated zirconia on the surface of TS-1.

EXPERIMENTAL

TS-1 containing 1% mol of titanium was prepared according to a procedure described earlier by Taramasso *et al.* [1]. Zirconium sulfate containing TS-1 was prepared by wet impregnation method. The TS-1 was added into a solution of zirconium sulfate hydrate $[\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}]$ in water. The mixture was stirred at room temperature for 3 h, followed by evaporation of the solvent at 100°C. The solid was then dried at 100°C for 24 h and calcined at 500°C for 7 h. The resulting sample was denoted as XZS/TS-1, in which X was the percentage of zirconium in the sample. For comparison, unsulfated zirconia impregnated TS-1 (sample 20Zr/TS-1, Zr=20 wt.%) was prepared by impregnation of TS-1 with zirconium isopropoxide from its hexane solution at room temperature. Then, the zirconium isopropoxide was hydrolyzed followed by drying at 100°C and calcination at 500°C for 7 h. Sample ZS500 was prepared by drying of zirconium sulfate hydrate at 100°C for 3 days followed by calcination at 500°C for 7 h.

All samples were characterized by powder X-ray diffraction (XRD) for crystallinity and phase content of the solid materials, using Bruker Advance D8 Diffractometer with the $\text{CuK}\alpha$ ($\lambda=1.5405 \text{ \AA}$) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. Infrared (IR) spectra of the samples were collected on a Shimadzu Fourier Transform Infrared, with a spectral resolution of 2 cm^{-1} , scanned every 10 s at 20°C. For the acidity study, the wafer of the sample (10-12 mg) was prepared and locked in the cell equipped with CaF_2 windows, and evacuated at 400°C under vacuum for 4 h. Pyridine was adsorbed at room temperature. Diffuse reflectance UV-visible (UV-vis DR)

spectra were recorded under ambient conditions on a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer. The spectra were monitored in the 190 – 600 nm range and Kubelka-Munk axis.

The catalysts performance was tested in the epoxidation of 1-octene using hydrogen peroxide (30%) as an oxidizing agent. The reaction mixture, i.e. 8 mmol of 1-octene, 15 mmol of H₂O₂ in 10 gram acetone as solvent and 0.8 mmol of cyclooctane as an internal standard were put in the round bottom flask equipped with a condenser. An amount of 0.05 g catalyst was then added into the solution. The reaction was carried out in an oil bath with stirring at 70°C. The products of the reaction were analyzed by Hewlett Packard Model 6890N gas chromatograph using Ultra-1 column and Hewlett Packard GC-MSD using HP5 column.

RESULTS AND DISCUSSION

Zirconium sulfate (ZS) at various contents was dispersed on TS-1. The XRD pattern of all the ZS/TS-1 samples showed that diffraction lines for tetrahedral or monoclinic phases of zirconia were not observed, which indicated that the ZS was highly dispersed on the surface of the TS-1. It is found that the MFI structure of TS-1 was still maintained after ZS loading (data not shown). However, the XRD peak intensities of TS-1 decreased as the loading amount of the ZS increased. This might be due to the decrease in the percentage amount of the TS-1 in the samples as the loading amount of the ZS increased. The monolayer coverage of zirconium can be determined from the graph of the diffraction line intensity of TS-1 at $2\theta=23^\circ$ vs. loading amount of zirconium on the samples. The diffraction lines of samples 2ZS/TS-1 and 5ZS/TS-1 showed similar intensities compared to the parent TS-1, while samples 10ZS/TS-1, 15ZS/TS-1 and 20ZS/TS-1 showed lower intensities. Hence, a horizontal line was found for low ZS loading and another straight line can be drawn for higher ZS loading. The intercept of the two lines occurred at the value $0.65 \text{ Zr}^{4+}/\text{nm}^2$ TS-1, which is equal to 6 wt.%. This value corresponds to the value for monolayer dispersion capacity of zirconium on the TS-1.

Figure 1a shows the IR spectra of the ZS/TS-1 samples after evacuation at 400°C for 4 h in vacuum. In the region of hydroxyl groups ($4000\text{--}3000 \text{ cm}^{-1}$), the peak of silanol groups at 3745 cm^{-1} still can be observed for samples with low loading amount of the ZS (2ZS/TS-1 and 5ZS/TS-1). However, the peak disappeared for samples with higher ZS loading (10-20ZS/TS-1). This finding suggests that the monolayer coverage of the ZS on the TS-1 is in the range of 5 to 10 wt.% of zirconium (0.57 to $1.12 \text{ Zr}^{4+}/\text{nm}^2$ TS-1), in which all silanol groups or surface of TS-1 have been covered with ZS with the maximum amount of $1.12 \text{ Zr}^{4+}/\text{nm}^2$ TS-1. The FTIR spectra of the ZS/TS-1 samples in the

ranges of $1700 - 1300 \text{ cm}^{-1}$ (Fig. 1b) show that samples 2ZS/TS-1, 5ZS/TS-1, and 10ZS/TS-1 exhibit a similar pattern, without the peak assigned for sulfate vibration. However, samples 15ZS/TS-1 and 20ZS/TS-1 showed additional peaks at 1370 cm^{-1} , assigned for asymmetric $\nu_{\text{S=O}}$, confirming the presence of sulfate species [7]. In addition, the intensity of this peak was significantly higher in sample 20ZS/TS-1, in which the amount of sulfate increased as ZS loading increased.

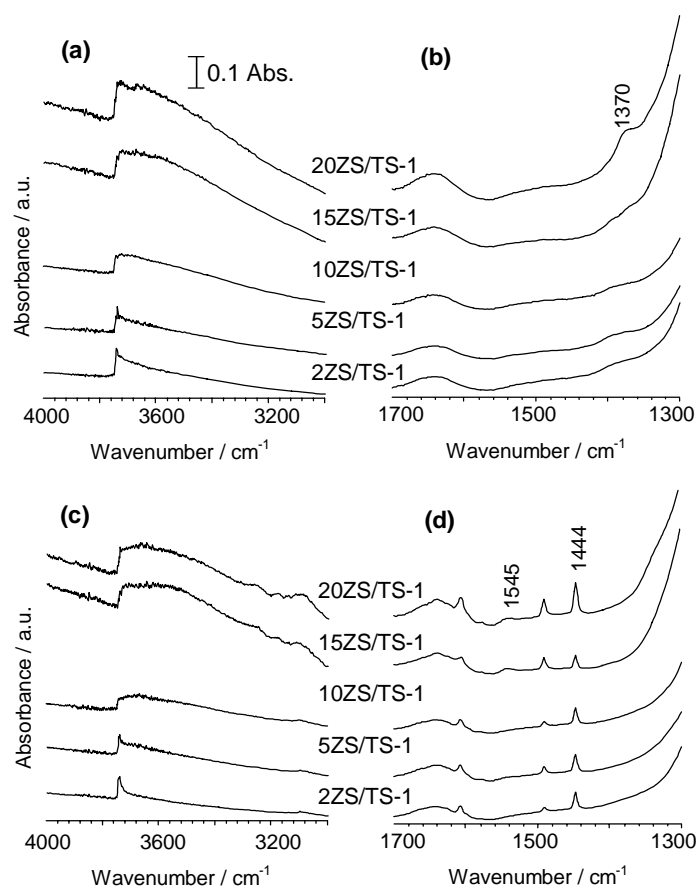


Fig. 1. FTIR spectra of the samples: (a, b) after evacuation at 400°C for 4 h in vacuum, (c, d) after pyridine adsorption and evacuation at 150°C for 1 h

It is interesting to relate the surface coverage of zirconium sulfate from the XRD finding with that of the IR spectroscopy. The XRD data found that the monolayer dispersion was $0.65 \text{ Zr}^{4+}/\text{nm}^2$ TS-1, while IR data had shown that the asymmetric $\nu_{\text{S=O}}$ appeared on sample 15ZS/TS-1 ($1.76 \text{ Zr}^{4+}/\text{nm}^2$ TS-1), but not for sample 10ZS/TS-1 ($1.12 \text{ Zr}^{4+}/\text{nm}^2$ TS-1). At the value of $1.12 \text{ Zr}^{4+}/\text{nm}^2$ TS-1, the asymmetric $\nu_{\text{S=O}}$ did not appear although this sample had almost double the zirconium content compared to the amount of zirconium monolayer dispersion capacity obtained from the XRD data *i.e.* $0.65 \text{ Zr}^{4+}/\text{nm}^2$ TS-1. The asymmetric $\nu_{\text{S=O}}$ only started to appear in samples at $1.76 \text{ Zr}^{4+}/\text{nm}^2$ TS-1, which contained more zirconium than that of double monolayer capacity. It can be suggested that the second layer coverage will be formed after the formation of monolayer on the solid support. Therefore, it can be proposed that the asymmetric $\nu_{\text{S=O}}$ started to appear on samples of ZS/TS-1 that contained double layer of ZS which was equal to $1.3 \text{ Zr}^{4+}/\text{nm}^2$ TS-1.

The spectra of the sample after pyridine adsorption in the region of hydroxyl groups are shown in Fig. 1c. There were no significant changes of the spectra as compared to that before pyridine adsorption. The silanol peak was still present after pyridine adsorption, indicating that the silanol groups did not react with pyridine. It is therefore concluded that the silanol groups are not acidic. In the regions of pyridine and sulfate as displayed in Fig. 1d, samples 2ZS/TS-1, 5ZS/TS-1 and 10ZS/TS-1 showed similar peaks at 1608 and 1444 cm^{-1} . These bands appeared when adsorbed pyridine bound coordinatively with Lewis acid sites in which these samples have similar amount of Lewis acid sites. These results indicated that zirconium was not responsible for the formation of Lewis acid sites. Meanwhile, samples 15ZS/TS-1 and 20ZS/TS-1 showed the absorption bands at 1640 and 1545 cm^{-1} , which corresponded to pyridine interacting with the Brönsted acid sites, beside bands at 1608 and 1444 cm^{-1} characteristic for Lewis acid sites. In addition, the peak for asymmetric $\nu_{\text{S=O}}$ disappeared after the adsorption of pyridine, indicating that the S=O was bound to pyridine. This finding suggests that the S=O acted as an active acid site. It also indicates that ZS was responsible for the formation of Brönsted acid sites and they were only present in samples containing a double layer of zirconium, whereas samples with a monolayer of zirconium did not show Brönsted acid sites. It is therefore concluded that sulfate can only bond with zirconia at the double layer of zirconium.

The UV-Vis DR spectrum of sample ZS500 indicated the existence of a shoulder band at around 210 nm and a sharp band centered at 230 nm (data not shown). A single absorption band at 210 nm can be observed on samples ZS/TS-1 containing low amount of zirconium (2, 5 and 10 wt.%), while a band at 225 nm was observed on samples 15ZS/TS-1 and 20ZS/TS-1. The band at around 210 nm is assigned for zirconium or titanium with tetrahedral coordination. The second band at lower energy at about 230 nm is attributable

to zirconium species in an octahedral coordination. The IR and UV-Vis DR data showed that both sulfate and octahedral zirconium species can only be observed on the samples containing double layer zirconium. From these, we can conclude that sulfate species bonded with the octahedral zirconium species and not with tetrahedral zirconium species. Clearfield *et al.* [8] have proposed a model that allowed for the formation of Brönsted acid sites on sulfated zirconia containing octahedral zirconium species after heating at 300°C.

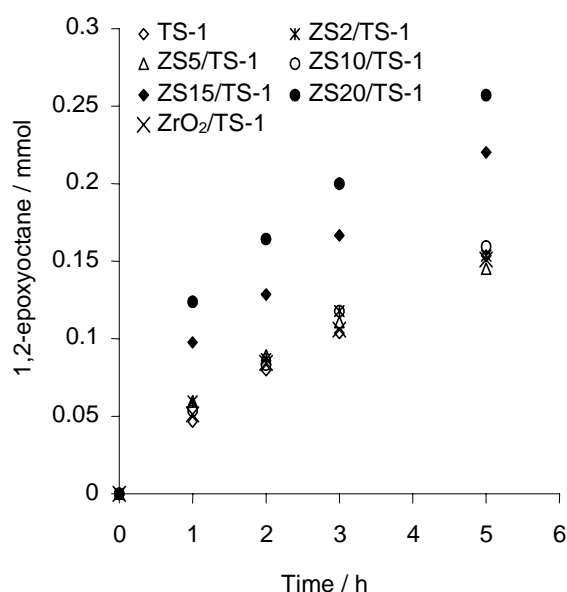


Fig. 2. The yield of 1,2-epoxyoctane on the epoxidation of 1-octene using various modified titanosilicalite-1 samples. All reactions were carried out at 70°C in acetone as solvent

All samples were tested as catalysts in 1-octene epoxidation using H₂O₂ as oxidant at 70°C. Figure 2 shows the rate of the formation of 1,2-epoxyoctane over various ZS/TS-1 samples. It can be seen that samples with low zirconium loading (2ZS/TS-1, 5ZS/TS-1 and 10ZS/TS-1) did not show any significant changes to the rate of reactions towards the formation of 1,2-epoxyoctane compared with TS-1 and ZrO₂/TS-1. However, remarkably higher activities were shown by samples at higher zirconium loading, ZS15/TS-1 and ZS20/TS-1. In addition, the 1,2-octanediol as by-product was observed, due to Brönsted acid sites present in the samples. This lowered the selectivity towards 1,2-epoxyoctane.

To determine the factor that influenced the enhancement of the catalyst activities, several experiments have been conducted. Higher activities were observed on samples ZS15/TS-1 and ZS20/TS-1. The characterization results showed that both samples contained high zirconium loading, Brönsted acid sites, octahedral zirconium, and sulfate species. However, from the catalytic testing, it was shown that the TS-1 containing high loading of zirconium without sulfate species (sample $\text{ZrO}_2/\text{TS-1}$) showed similar reaction rates with TS-1 itself, while the addition of HZSM-5 zeolite that contained Brönsted acid sites did not show significant changes of reaction rates. The structures of zirconium species present in the samples also did not influence the catalytic activity of the parent catalyst. When ZS500 was used as a catalyst without TS-1, no epoxidation product was obtained. Thus, high zirconium loading, Brönsted acid sites, octahedral zirconium containing ZS/TS-1, and ZS were not directly contributing to the enhancement of the catalytic activity. Therefore, it is suggested that the enhancement of its catalytic activity can be attributed to the sulfate-bonded zirconia species present in the surface of TS-1.

For olefin epoxidation reaction using H_2O_2 catalyzed by TS-1, the reactive sites are oxo-titanium species (superoxo- and hydroperoxo-titanium) [9]. The reactive oxo-titanium species in TS-1 were generated by the interaction of tetrahedral titanium (tetrapodal or tripodal) in TS-1 with aqueous H_2O_2 adducts. It was also reported that solvent acetone retarded the formation of oxo-titanium species [9]. Therefore, in this study, the increase of epoxidation reaction rates using ZS/TS-1 catalysts can be explained by the rates of the formation of the reactive oxo-titanium species. It is known that TS-1 has hydrophobic properties, while ZS has hydrophilic properties. The sulfate present on the surface of ZS/TS-1 probably can increase the adsorption rate of aqueous H_2O_2 into TS-1. Consequently, the rate of the formation of oxo-titanium species increased and accordingly the production of epoxides are also increased.

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