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Synthesis, characterization and catalytic properties of TS-1 monoliths

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Titanium silicalite-1 monolith (TS-1M) was prepared using polyurethane foam as the template. The characterization of the TS-1M was carried out using XRD, SEM, UV–vis and FT-IR spectroscopies, and water vapor adsorption. Catalytic activity was measured for 1-hexene and 2,5-dihydrofuran epoxidation using H_2O_2 as an oxidant. These studies revealed that TS-1 monoliths have essentially identical chemical properties to the TS-1 powders, but the crystal morphology was different and diffusion plays an important role in the catalysis of the liquid-phase epoxidation reactions.

KEY WORDS: TS-1 monolith; 2,5-dihydrofuran; 1-hexene; epoxidation; diffusion effects; crystal morphology.

1. Introduction

Titanium silicate-1 discovered by Enichem [1] is a redox molecular sieve with MFI structure, in which isolated titanium sites in the zeolite framework act as active sites for the oxidation of a variety of organic substrates using H_2O_2 as oxidant. TS-1 is known to catalyze aromatic hydroxylation, alkene epoxidation, ketone ammoximation, alcohol and alkane oxidation, and initiated an intense research activity on redox molecular sieves.

3,4-Epoxytetrahydrofuran (3,4 ETHF) is an important building block for the synthesis of substituted tetrahydrofurans, which are useful organic compounds especially in pharmaceutical and agrochemical applications as stereochemical control elements [2]. Currently, the preparation of 3,4 ETHF has been reported through the oxidation of 2,5 dihydrofuran (2,5 DHF) using strong peracids, which causes environmental concern [3]. As a more environmentally acceptable synthesis method of 3,4 ETHF, it was established by us that 3,4 ETHF can be prepared in high yield via heterogeneous epoxidation of 2,5 DHF using TS-1 [4]. In order to produce 3,4 ETHF in a large scale, the conduction of the reaction in a continuous rather than a batch mode is being considered. For this purpose, TS-1 was formed into a single piece of monolith using polyurethane foam (PUF) as a template to produce a rigid, self-supporting catalyst without adding any inorganic binders to implement in a tubular reactor. The original forming process for silicalite-1 monolith by Lee *et al.* [5] was extended here to TS-1.

In this contribution, comparison of physicochemical properties of the TS-1 monolith catalysts with the TS-1 powder prepared according to the original Enichem recipe [1] was conducted; essential characterization using XRD, SEM, UV–vis and FT-IR spectroscopies were performed and 1-hexene epoxidation was chosen as the probe reaction. Finally, epoxidation of 2,5 DHF was carried out in batch mode to compare the performances of two different types of TS-1 catalysts.

2. Experimental

The typical procedure for TS-1 monolith is as follows: 10 g of tetraethyl orthosilicate (TEOS) was hydrolyzed in a solution of tetrapropylammonium hydroxide (TPAOH) (1 M, Aldrich, 6.25 mL) and 59 mL of H_2O under magnetic stirring. Then, 0.13 g of titanium isopropoxide in isopropanol (3 mL) was added dropwise to the solution. The molar ratio of the final gel was $Si:TPAOH:Ti:H_2O = 5:1:0.05,\ 0.10:350$. Two samples with $Ti/Si = 0.01$ and 0.02 were prepared. Polyurethane foam (PUF) template was fully soaked into the final clear gel by squeezing the foam. The density of the PUF used was 0.0212 $g cm^{-3}$. Hydrothermal reaction was carried out at 453 K for 2 days. Finally, TS-1 monolith was thoroughly washed with distilled water and calcined at 823 K for 12 h under flowing oxygen. 2% TS-1 powder reference catalyst was also prepared by the literature process [1], which will be designated as TS-1R (2%) in this work.

The crystallinity of the sample prepared was measured by X-ray diffraction using Ni-filtered Cu Kα radiation (Philips, PW-1700), and the morphology of the samples was examined by SEM (Hitachi, X-650). FT-IR spectra were recorded in air at room temperature on a Bomem MB 104 spectrometer using a diffuse reflectance cell. UV–vis diffuse reflectance spectroscopy was performed under ambient conditions using dehydrated MgO as a reference

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in the range of 190–800 nm on a Varian CARY 3E double-beam spectrometer. Water vapor adsorption on TS-1 samples was measured using Quantachrome Autosorb Automated Gas Sorption System. Samples were degassed at 573 K for 4 h and the sorption measurement was conducted at 300 K. The catalytic activities of all the samples were tested for 1-hexene and 2,5-dihydrofuran epoxidation using H_2O_2 as an oxidant. 1-hexene epoxidation was carried out under vigorous stirring in a two-neck pyrex reactor equipped with a condenser and a thermometer using 2.02-g substrate, 150-mg catalyst, 25-mL methanol as a solvent, and 0.65 g of 35 wt% H_2O_2. The reaction was conducted at 313 K for 2 h and the product was analyzed using a GC equipped with a Supelco capillary column and an FID. For 2,5-dihydrofuran (2,5 DHF) epoxidation, the mixture of 2,5 DHF, solvent and TS-1 was put into a 500-mL round bottom flask equipped with a reflux condenser, and was heated in an oil bath with vigorous stirring. Reaction was commenced by introducing H_2O_2 (aqueous, 30 wt%) to the reaction mixture and terminated after 12 h of reaction. H_2O_2 was introduced dropwise in 1 h duration using a syringe pump. Reaction conditions were 0.002 mole 2,5 DHF, 0.00 28 mole H_2O_2 (30 wt% solution), 100 g solvent, and 0.5 g TS-1 at 338 K. Product samples were taken every 2 h and the contents were analyzed using HP 6890 GC equipped with FID and HP-PONA column. The H_2O_2 that remained after the reaction was determined by cerium sulfate titration [6].

3. Results and discussion

After hydrothermal treatment of the PUF template soaked with the TS-1 clear gel mixture at 453 K for 2 days, a cylindrical monolith of a porous light inorganic material was formed. Figure 1 shows the photograph of the TS-1 monolith (TS-1M) and SEM micrographs of the details. The shape and size of the TS-1M was almost identical with those of the PUF template. The SEM image of the cross sections of the TS-1M struts reveal the remarkable fact that the whole body of the monolith, in fact, consists of a single piece of a very thin TS-1 film shaped into a discrete architecture of open macroporous cells and struts. The triangular cross sections of the struts also precisely resemble those of PUF, which indicates that the PUF template decomposed slowly within the interior of the surface covering the TS-1 film in a strongly basic medium. The color of the inorganic material was pale yellow due to the presence of decomposed fragments of PUF within the interconnected macropore channels in the monolith, which was mostly removed by a simple washing with water or acetone and more completely by calcinations at 823 K for 12 h under flowing oxygen. The density of the calcined TS-1 monolith was ca. 0.016 $g cm^{-3}$. Methanol passes readily through the TS-1 monolith, and the three-dimensional body structure was maintained after an overnight immersion in excess methanol.

Physicochemical properties of the TS-1 monolith were evaluated subsequently, compared with the reference TS-1R, to make sure that no detrimental effect of the potential impurities is present in catalytic applications. Figure 2 shows the XRD patterns of TS-1 monoliths ground to fine powders. All the samples showed peaks corresponding to the characteristic of MFI structure with almost identical peak intensities. Figure 3 shows IR (A) and UV–vis (B) spectra of the samples. A characteristic IR band at 960 cm^{-1} corresponding to the Si–O–Ti bond [7] is observed in all samples. The relative intensity of the 960 cm^{-1} to 800 cm^{-1} peak has often been used to estimate the titanium incorporation in TS-1 samples [8]. The characteristic absorption band at ca. 220 nm indicating titanium in tetrahedral coordination [9] is clearly shown in UV–vis spectra as well. No peaks corresponding to anatase phase at 330 nm or nano-phase TiO_2 clusters at 270 nm were observed. These characterization results demonstrate that monolith forming process using PUF do not result in any noticeable structural/chemical changes in TS-1. Figure 4 shows high-resolution SEM images of the TS-1R powder (2%) and TS-1M (1, 2 mol%) in ground form. A coffin-shaped crystal with average size of 2 μm is clearly visible for 2% TS-1M,

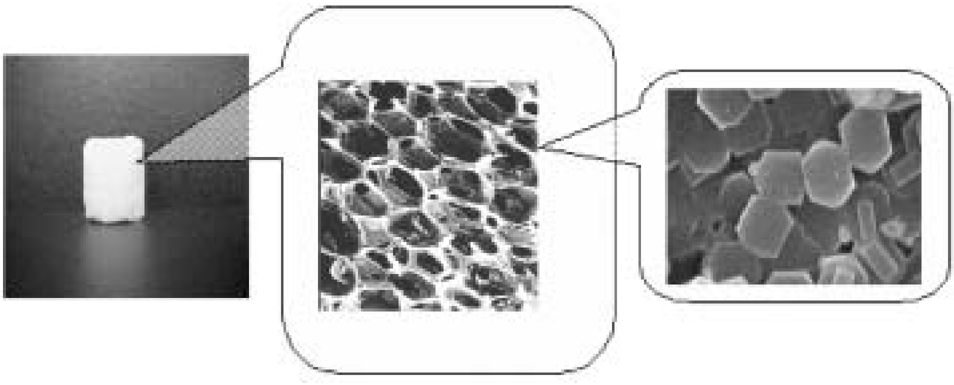


Figure 1. SEM micrograph of TS-1M (2%).

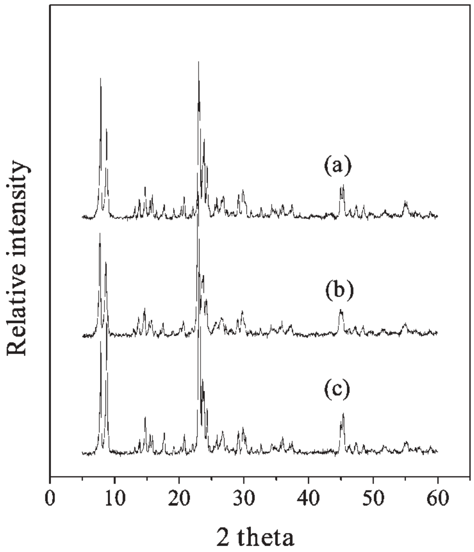


Figure 2. XRD spectra of (a) TS-1R (2%), (b) TS-1M (1%), (c) TS-1M (2%).

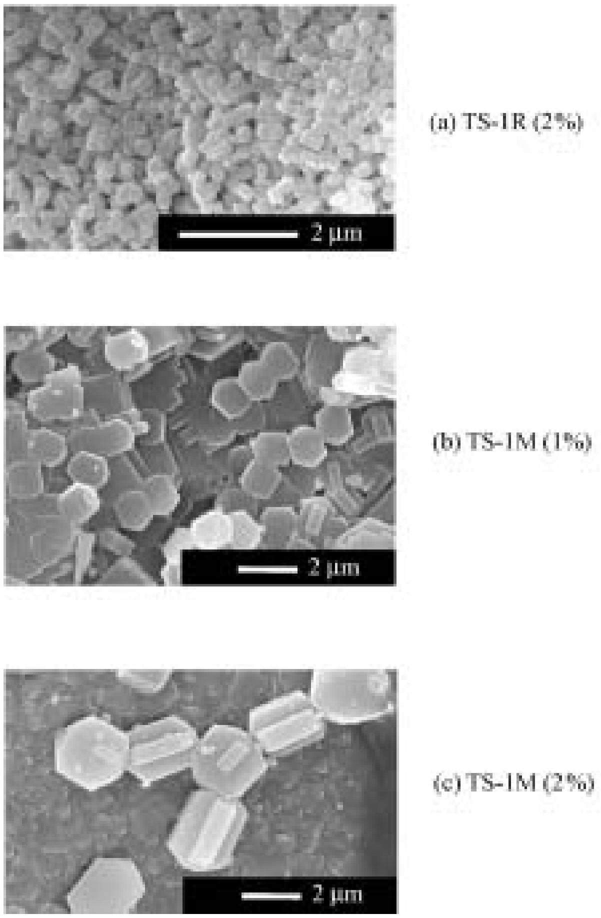


Figure 4. SEM micrographs of TS-1.

whilst the average crystal size decreased to ca. 1 μm in 1% TS-1M. This is in sharp contrast to the more square-shaped crystals with an average size of 0.3 μm for TS-1R (2%) powder. Such differences in the crystal size of a microcrystalline zeolite can have an important bearing in catalytic activity [10] and also in selectivity [11] owing to different diffusion paths.

In order to evaluate the hydrophobicity of TS-1 monoliths, water adsorption isotherms were measured. As shown in figure 5, the tested TS-1 samples were all very hydrophobic with only a small amount of water (ca. $0.05\,\mathrm{cm}^3\,\mathrm{g}^{-1}$) being adsorbed even at a relative partial pressure near 1.0. Ti(IV) in TS-1 is accessible to interaction with small polar molecules and forms six-coordinated complexes by ligand insertion in Ti(IV) coordination sphere [12]. Thus, TS-1M (2%) was found to be slightly less hydrophobic than TS-1M (1%) because of the higher amount of titanium available for water adsorption. Little difference in water adsorption capacity between TS-1M (2%) and TS-1R (2%) was observed, again confirming that the surface properties of both the samples are virtually identical.

Catalytic property of the TS-1 monolith samples was initially tested by the well-known probe reaction of

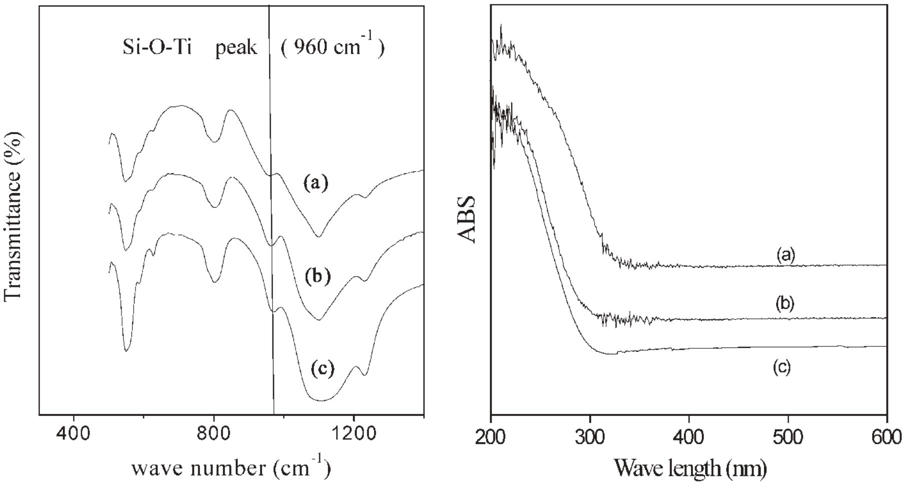


Figure 3. IR (A) and UV–vis (B) spectra of (a) TS-1R (2%), (b) TS-1M (1%), (c) TS-1M (2%).

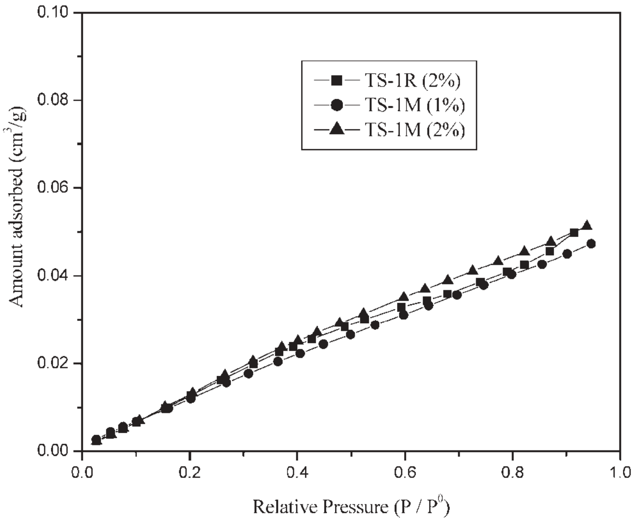


Figure 5. Water adsorption isotherms for TS-1 samples.

1-hexene epoxidation using H_2O_2, and the experimental results are summarized in table 1. The catalytic activity order was found to be 2% TS-1R (13.8% conversion) > 2% TS-1M (11.3%) > 1% TS-1M (8.5%). The H_2O_2 selectivity measured by cerium sulfate titration method showed almost 100% selectivity in all cases, indicating that no unproductive H_2O_2 decomposition took place. According to SEM-EDS analysis, both TS-1R (2%) and TS-1M (2%) had close to 2% titanium loadings within the instrument accuracy. Therefore, the difference in conversion between 2% TS-1 catalysts is most likely to be a consequence of the different crystal sizes mentioned above; larger crystals of TS-1M causing slower diffusion of 1-hexene than the reference TS-1 powder.

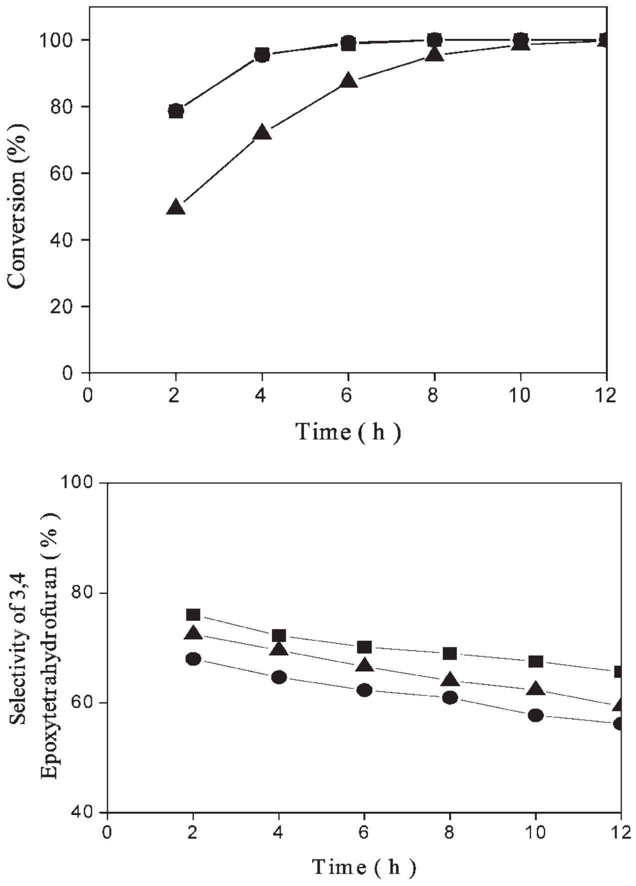


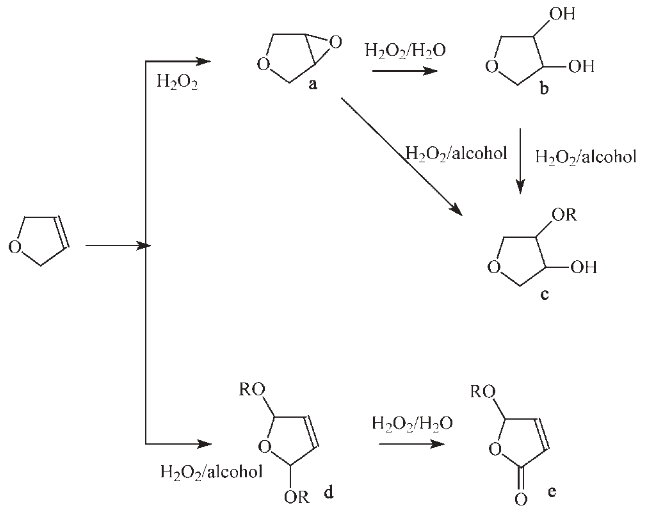
Figure 6. Conversion and selectivity profiles of 2,5-dihydrofuran epoxidation. (■: TS-1R (2%); ▲: TS-1M (1%); ●: TS-1M (2%)) Reaction condition: 500-mg catalyst; 10 g, 2,5-dihydrofuran; 22.8 g, 30% H_2O_2; 100 g, methanol; 343 K.

Table 1
1-Hexene epoxidation

TS-1 sample	1-Hexene conversion (%)	H_2O_2 conversion (%)	H_2O_2 selectivity (%)
TS-1R (2%)	13.8	41.4	100
TS-1M (2%)	11.3	34.8	100
TS-1M (1%)	8.5	27.4	100

Note: Reaction condition: 150-mg catalyst; 2.02 g, 1-hexene; 0.65 g, 30% H_2O_2; 19.78 g, methanol (313 K; reaction duration 2 h).

Finally, TS-1M (1, 2%) catalysts were tested as epoxidation catalysts for 2,5-dihydrofuran (2,5 DHF), and the results are shown in figure 5. 3,4-epoxytetrahydrofuran (3,4 ETHF) was the main product and 3,4-dihydroxytetrahydrofuran and its alkyl ester were formed as the by-product. Allylic oxidation products of 2,5 dihydro-2,5-dialkoxyfuran and 2,5 dihydro-5-alkoxy-2-furanone were also found. A proposed mechanism of 2,5 DHF oxidation using H_2O_2-TS-1–solvent system is shown in scheme 1. In this case, catalytic activity of TS-1M was virtually the same as that of TS-1R powder at the same titanium loading of 2%. It seems that 2,5 DHF is less sterically demanding than 1-hexene, which showed a minor conversion difference (see table 1). 1% TS-1M was less active as



Scheme 1. Proposed mechanism of 2,5 DHF oxidation using H_2O_2-TS-1–solvent system.

expected, but all the TS-1 catalysts tested achieved close to 100% conversion after 10 h reaction in batch mode. Higher selectivity to 3,4 ETHF was, however, obtained following the sequence of TS-1M (2%) < TS-1M (1%) < TS-1R (2%), which corresponds to the order of decreasing TS-1 particle size. TS-1 with larger particle size is expected to produce a longer diffusion path for 3,4 ETHF, exposing it to ring opening and further oxidation taking place on the way out from the pore interior. In accordance with this proposal, (b, c, e) in scheme 1 were found to increase in the sequence of TS-1R (2%) < TS-1M (1%) < TS-1M (2%). Thus, the particle size did affect the product distribution in this case. Further work is in progress to control the particle morphology of TS-1M by optimizing the catalyst preparation process.

4. Conclusions

Titanium silicalite-1 monolith was prepared using polyurethane foam as a template. It was established that TS-1 monolith has essentially identical chemical properties to TS-1 powders, but crystal morphology was different in that diffusion played an important role in catalytic applications. Both catalytic activity and selectivity in 2,5-dihydrofuran epoxidation were somewhat less using monolithic TS-1 than TS-1 reference powder owing to the substantially larger crystals in the TS-1 monolith.

Acknowledgments

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