

# The Synthesis of Mesoporous TS-1 and Its Performance for Oxidation of Diphenyl Sulfide and Dibenzyl Sulfide

Hua-Qin Wang<sup>1</sup>, Ya-Long Ding<sup>1\*</sup>, Pei Yu<sup>1</sup>, Ya-Meng Li<sup>1</sup>, Hai-Xiang Gao<sup>1</sup>, Wen-Jie Sun<sup>1</sup>, Meng-Die Chen<sup>1</sup> and Rong-Qiang Li<sup>1\*</sup>

<sup>1</sup>College of Chemistry and Pharmaceutical Engineering, Huanghuai University, Zhumadian, Henan, 463000, China

**Abstract.** TS-1 zeolite has outstanding performance in the catalytic reactions with hydrogen peroxide as catalytic promoter. However, the narrow pore size (< 1.0 nm) of traditional TS-1 makes it difficult for bulky organic compounds to contact with the active sites in the pores, which seriously limits application of TS-1. Recently, the introduction of mesoporous structure into microporous TS-1 becomes a hot research topic. Meanwhile, the huge synthesis cost of TS-1 is another main reason hindering its industrial application. In this paper, mesoporous TS-1 was successfully synthesized using sodium silicate as silicon source and titanium trichloride as titanium source under the template conditions of tetrapropylammonium hydroxide (TPAOH) and cationic polymer. The mesoporous TS-1 was characterized by X-ray diffraction (XRD), N<sub>2</sub> adsorption, scanning electric microscopy (SEM), transmitting electric microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR) and UV-Vis Spectrum spectra (UV-Vis). Results show that the synthesized TS-1 zeolites have good crystallinity and tetra-coordinated framework Ti atoms, and there are abundant mesoporous structures in the zeolite crystals. The results of oxidation experiments show that conversion of diphenyl sulfide and dibenzyl sulfide with mesoporous TS-1 are 97.3 % and 85.3 % respectively, while that conversion with microporous TS-1 are 75.7 % and 63.5 % respectively.

## 1. Introduction

As one titanium silicalite zeolite, TS-1 has attracted wide attention due to its excellent catalytic performance in selective oxidation and epoxidation with hydrogen peroxide as oxidant[1]. However, the small pore size of traditional TS-1 limits its application in bulky molecule catalytic conversion, and the high cost greatly restricts its application in industrial production. Recently, mesoporous structure has been successfully introduced into microporous TS-1 crystals using various carbon materials as hard templates[2]. Besides, Choi[3] synthesized porous titanium silicalite catalytic materials by using expensive multi head quaternary ammonium salt surfactant as soft template method. However, expensive organosilicon sources (TEOS) and a large number of organic titanium sources (tetrabutyl titanate, TBOT) were used in the synthesis system, and a large number of small molecular template, such as tetrapropyl ammonium hydroxide (TPAOH) were used. All these items cause the high cost of TS-1 zeolite. It has been reported that microporous TS-1 zeolite can be synthesized by using cheap inorganic silicon sources (such as silica sol) and titanium sources (such as titanium trichloride and titanium sulfate) in the presence of TPAOH [4,5]. But the synthesis of mesoporous TS-1 using inorganic silicon and titanium sources has always been an unsolved problem.

With the continuous deterioration of the environment and the continuous enhancement of people's awareness of environmental protection, requirements for low sulfur in petroleum products are increasingly strict[6]. Meanwhile, desulfurization is also one of the hot spots and difficulties in the petroleum processing industry. Among the numerous desulfurization methods, oxidative desulfurization has attracted great attention due to its mild conditions, short reaction time and high desulfurization degree, especially for the high-efficiency removal of sulfide which is difficult to remove in conventional hydrodesulfurization technology[7].

In this paper, TS-1 with mesoporous structure was synthesized by using self-developed cationic polymer as template, sodium silicate as silicon source and titanium trichloride as titanium source. And the catalytic oxidation of bulky organic compounds (diphenyl sulfide and dibenzyl sulfide) was studied.

## 2. Experiments

### 2.1. Synthesis of self-developed cationic polymer (MCCM)

In a typical run, 4.5 g diallylamine (99 wt.%), 35 g dimethyldiallylammonium chloride solution (50 wt.% in water), 20 g pure water and 4.5 g acetic acid were mixed in a flask. After the solution was stirred at 25 °C for 30

\* Corresponding author: [dingyalong@huanghuai.edu.cn](mailto:dingyalong@huanghuai.edu.cn); [rqli@iccas.ac.cn](mailto:rqli@iccas.ac.cn)

mins, 10 g of ammonium persulfate solution (5 wt.% in water) was dropped into the reaction system. Then the final solution was heated to 100 °C and maintained for 4 hours, and then cooled to 25 °C to obtain the desired mesoporous template MCCM.

## 2.2.Synthesis of microporous TS-1 and mesoporous TS-1

(1) Synthesis of microporous TS-1: 0.2 g TBOT was added slowly to 6.0 mL TEOS solution under stirring, then the obtained transparent solution was added drop by drop into another solution containing 4.8 mL TPAOH (25 wt.% in water) and 3 mL isopropanol. What should be noted is that precipitation is not allowed to occur during the dropping process. Then, 21.0 mL water was added and stirred for 3 hours. After that, the obtained transparent solution was heated in a 348 K water bath for 5 hours. The transparent solution, with materials ratio as 1.0SiO<sub>2</sub>/0.02TiO<sub>2</sub>/0.20TPAOH/50H<sub>2</sub>O, was obtained, and was put into an autoclave with polytetrafluoroethylene (PTFE) liner and hold at 180 °C for 3 days. Obtained sample was cooled, filtered and dried at 120 °C for 12 hours, and then roasted at 550 °C for 4 hours. Finally, the obtained white powder is microporous TS-1, labelled as TS-1.

(2) Synthesis of mesoporous TS-1: 6.5 mL TPAOH (25 wt.% in water) was added into the mixture of 10.0 mL water glass and 10.0 mL H<sub>2</sub>O, and stirred strongly for 1 hour. Then, 6.0 mL of mesoporous template MCCM and the mixture of 0.97 g TiCl<sub>3</sub> and 20.0 mL H<sub>2</sub>O were added dropwise, the final material composition is 1.0SiO<sub>2</sub>/0.02TiO<sub>2</sub>/0.15TPAOH/0.21Na<sub>2</sub>O/0.011MCCM/50H<sub>2</sub>O. After stirring for 3 hours, the obtained paste mixture was put into the autoclave with polytetrafluoroethylene (PTFE) liner and kept at 180 °C for 3 days. After cooling, the mixture was filtered and dried at 120 °C for 12 hours, and then roasted at 550 °C for 4 hours. Finally, the obtained white powder is mesoporous TS-1, labelled as MTS-1.

## 2.3.Characterization of MTS-1 and TS-1

The XRD patterns of samples were obtained on RIGAKU ultimaIV diffractometer with K $\alpha$  radiation from Cu target as source, the tube voltage and current was 40 kV and 40 mA respectively, and the scanning range was 5-50° with the scanning speed as 2 °/min. N<sub>2</sub> adsorption-desorption of the samples was performed on Micromeritics ASAP2020M analyser at liquid nitrogen temperature (-196 °C). The samples were pre-treated at 350 °C for 10 hours before N<sub>2</sub> adsorption-desorption analysis. The specific surface area of the sample was calculated by Barrett Emmett Teller (BET) method, and the pore size distribution was calculated by Barrett Joyner Halenda (BJH) method. The SEM images of the samples were obtained on NanoSEM200 with an operating voltage of 5 kV, and the TEM images were obtained on JEM-2100F with the information resolution limit of 1.4 Å and the operating voltage of 200 kV. FT-

IR spectra of samples were obtained on Nexus870 instrument by KBr compression method, and UV-Vis spectra were obtained on Perkin-Elmer Lambda25 spectrometer.

## 2.4.Catalytic performance of MTS-1 and TS-1

The catalytic oxidation performance of MTS-1 and TS-1 for bulky molecules diphenyl sulfide and dibenzyl sulfide was carried out in a 50 ml round bottomed flask with reflux. The reactions were carried out at 50 °C for 5 hours. Specifically, 20 mg catalyst (MTS-1 or TS-1), 500 mg diphenyl sulfide (or dibenzyl sulfide), 6 mL methanol and 0.2 mL H<sub>2</sub>O<sub>2</sub> (30 wt.% in water) were added into the reactor, and then put into the oil bath at 50 °C. After the reactions, 0.4 g Na<sub>2</sub>SO<sub>3</sub> was added to the reaction tube to consume the remaining H<sub>2</sub>O<sub>2</sub>. The catalyst was removed by centrifugation and the liquid samples were analysed by gas chromatography (Agilent 7890A) with FID detector.

## 3.Results and discussion

### 3.1.Characterization of MTS-1 and TS-1

The XRD spectra of MTS-1 and TS-1 were shown in Figure 1. It can be seen that MTS-1 and TS-1 have five typical diffraction peaks of MFI topology at 2 $\theta$  = 7.8°, 8.8°, 23.2°, 23.8° and 24.3°, and both MTS-1 and TS-1 sample has good crystallinity.

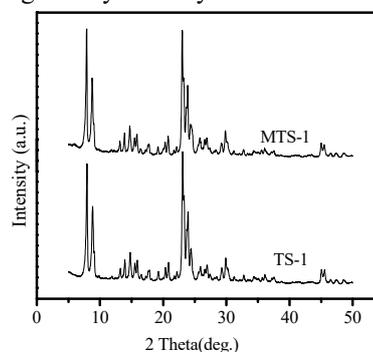


Figure 1 XRD spectra of MTS-1 and TS-1 sample.

Figure 2 shows the N<sub>2</sub> adsorption-desorption isotherm and pore size distribution of MTS-1. It can be seen that a hysteresis loop is formed in the range of relative pressure of 0.45-0.9, indicating the existence of mesoporous structure in MTS-1. The pore size distribution curve in the illustration shows that the mesoporous size is mainly concentrated at 11 nm. Detailed texture parameters of MTS-1 and TS-1 samples are given in Table 1. According to the data in Table 1, MTS-1 has large mesoporous surface area and mesoporous pore volume. Because the grains of TS-1 synthesized by using tetrabutyl titanate and tetrabutyl orthosilicate are generally small, so TS-1 also has a high outer surface, and the small mesoporous pore volume of TS-1 is mainly formed by the accumulation of particles.

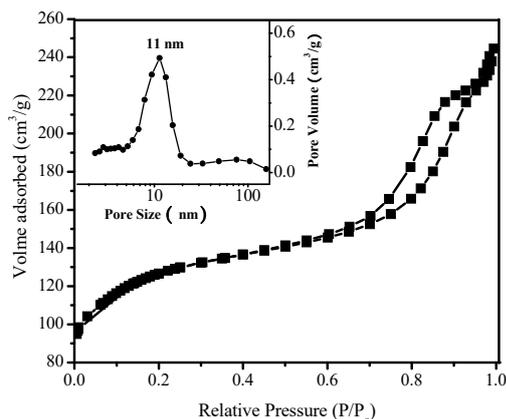


Figure 2 N<sub>2</sub> adsorption-desorption isotherm and pore size distribution of MTS-1

Table 1 Texture parameters of MTS-1 and TS-1 samples

Sample	BET surface (m <sup>2</sup> /g)	External surface (m <sup>2</sup> /g)	Microporous volume (cm <sup>3</sup> /g)	Mesoporous volume (cm <sup>3</sup> /g)
MTS-1	427	211	0.10	0.28
TS-1	411	140	0.13	0.09

Figure 3 shows the SEM and TEM images of MTS-1. It can be seen from the SEM image that MTS-1 has an elliptical grain shape, and the size is relatively uniform as 400-500 nm (Figure 3a). The TEM image of MTS-1 show that abundant mesopores are introduced into the zeolite crystal (bright spots are mesoporous pores, Figure 3b), and the pore diameter is about 10 nm, which is consistent with the pore size distribution obtained by N<sub>2</sub> physical adsorption.

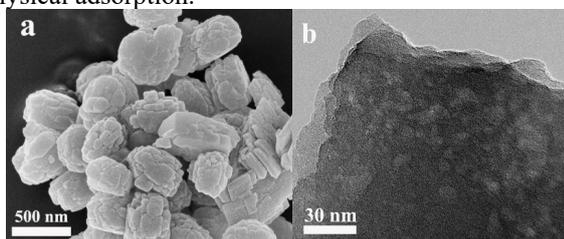


Figure 3 SEM (a) and TEM (b) images of MTS-1

Figure 4 shows the FT-IR and UV-Vis spectra of MTS-1 and TS-1 samples. In the FT-IR spectra (Figure 4a), the infrared absorption peaks at 1225, 1100, 800, 550 and 450 cm<sup>-1</sup> indicate the existence of MFI topological structure in zeolite [8,9]. The absorption peak at 960 cm<sup>-1</sup> is attributed to the vibration of Si-O bond caused by Ti atoms entering the framework of zeolites. But some researchers have pointed out that the absorption peak appears at 960 cm<sup>-1</sup> when other metal atoms (such as Fe, V, Cr, etc.) enter into the framework of zeolites instead of Ti atoms. Therefore, the absorption peak at 960 cm<sup>-1</sup> may be related to Si-OH or Ti=O bond or framework defect of zeolite. However, for TS-1 zeolites, the absorption peak at 960 cm<sup>-1</sup> can be used as the auxiliary evidence for Ti incorporation in zeolite framework [10,11,12]. The UV absorption spectra of the samples (Figure 4b) show that MTS-1 and TS-1 have strong absorption near 210 nm, indicating that the presence of tetra coordinated titanium species in zeolite framework [13-16].

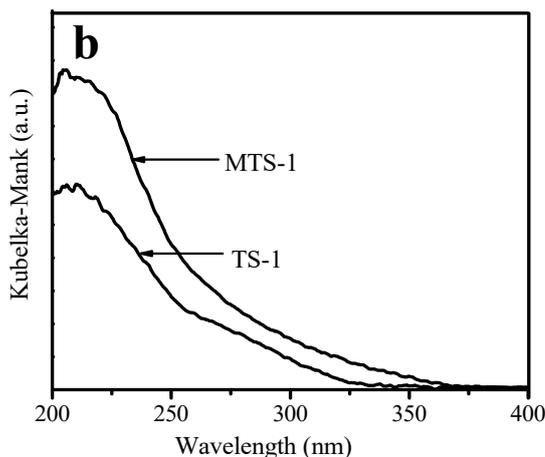
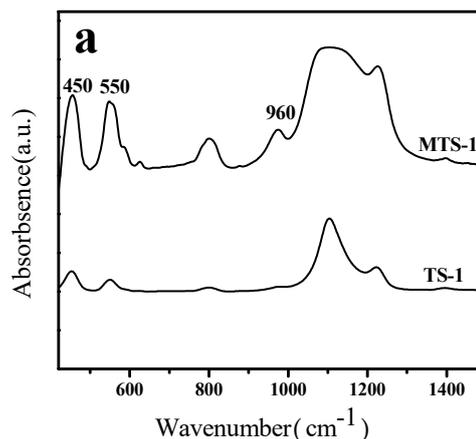


Figure 4 FT-IR spectra (a) and UV-Vis spectra (b) of MTS-1 and TS-1

Table 2 Catalytic performance of MTS-1 and TS-1 for diphenyl sulfide and dibenzyl sulfide

Sample	Substrate	Conversion n (%)	Selectivity (%)	
			RSO <sup>a</sup>	RSO <sup>b</sup>
MTS-1	diphenyl sulfide	97.3	59.8	40.2
TS-1	diphenyl sulfide	75.7	75.4	24.6
MTS-1	dibenzyl sulfide	85.3	93.9	6.1
TS-1	dibenzyl sulfide	63.5	97.5	2.5

<sup>a</sup> selectivity of sulfoxide

<sup>b</sup> selectivity of sulfone.

### 3.2. Catalytic performance of MTS-1 and TS-1

The comparison of catalytic oxidation performance of MTS-1 and TS-1 catalysts for diphenyl sulfide and dibenzyl sulfide is given in Table 2. The results showed that the conversion of phenyl sulfide and dibenzyl sulfide on MTS-1 catalyst was higher than that on TS-1 catalyst. This is because the mesoporous structure in MTS-1 catalyst is very conducive to the diffusion of these two bulky molecules. The conversion of diphenyl sulfide and dibenzyl sulfide on TS-1 catalyst is mainly due to the external surface of TS-1 resulting from its smaller particle diameter. In other words, for TS-1 catalyst, the reactions mainly carried out in the mesoporous channels of the zeolite, while for TS-1

catalyst, the reactions mainly take place on the outer surface of the zeolite.

## 4. Conclusion

In this paper, mesoporous TS-1 zeolite was synthesized by using sodium silicate and titanium trichloride as silicon and titanium sources, tetrapropyl ammonium hydroxide and cationic polymer as co-template. Various characterization results showed that the mesoporous structure was successfully introduced into the crystal of TS-1. The mesoporous TS-1 synthesized by this method has good crystallinity, and Ti species are effectively introduced into the framework structure of zeolite. Compared with microporous TS-1, mesoporous TS-1 has better catalytic activity in the oxidation of bulky organic molecules of diphenyl sulfide and dibenzyl sulfide.

We are grateful for the support of Key Projects of Universities in Henan Province (21B530004).

## References

- [1] A. Thangaraj, R. Kumar, P. Ratnasamy, *J. Catal.* **131**, 294 (1991)
- [2] Y. Fang, H. Hu, *Catal. Commun.* **8**, 817 (2007)
- [3] M. Choi, H. S. Cho, R. Srivastava, *Nat. Mater.* **5**, 718 (2006)
- [4] X. S. Wang, X. W. Guo, G. Li, *Catal. Today* **74**, 65 (2002)
- [5] M. Wang, J. Zhou, G. Mao, X. Zheng, *Ind. Eng. Chem. Res.* **51**, 12730 (2012)
- [6] L. Kong, G. Li, X. Wang, B. Wu, *Energ. Fuel* **20**, 896 (2006)
- [7] Z. Kang, G. Fang, Q. Ke, J. Hu, T. Tang, *ChemCatChem* **5**, 2191 (2013)
- [8] Q. Zhao, P. Li, D. Li, X. Zhou, W. Yuan, X. Hu, *Micropor. Mesopor. Mat.* **108**, 311 (2008)
- [9] A. Tuel, *Catal. Lett.*, (1998)
- [10] R. S. Drago, S. C. Dias, J. M. Mcgilvray, *J. Phys. Chem. B* **102**, 1508 (1998)
- [11] G. Ricchiardi, A. Damin, S. Bordiga, C. Lamberti, G. Spanò, F. Rivetti, Z. Adriano, *J. Am. Chem. Soc.* **123**, 11409 (2001)
- [12] W. Lin, H. Frei, *J. Am. Chem. Soc.* **124**, 9292 (2002)
- [13] S. B. Kumar, S. P. Mirajkar, G. C. G. Pais, P. Kumar, R. Kumar, *J. Catal.* **156**, 163 (1995)
- [14] J. F. Bengoa, N. G. Gallegos, S. G. Marchetti, A. M. Alvarez, M. V. Cagnoli, A. A. Yeramian, *Micropor. Mesopor. Mat.* **24**, 163 (1998)
- [15] L. Kong, G. Li, X. Wang, *Catal. Today* **93-95**, 341 (2004)
- [16] X. D. Wang, B. Q. Zhang, X. F. Liu, J. Y. S. Lin, *Adv. Mater.* **18**, 3261 (2010)