

The effect of T-atom ratio and TPAOH concentration on the pore structure and titanium position in MFI-Type Titanosilicate during dissolution-recrystallization process

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Abstract

In this work, titanosilicate MFI (TS-1) crystals with different Si/Ti ratio were treated with tetrapropylammonium hydroxide (TPAOH) solution of different concentrations. The results showed that the properties – crystal structure, titanium position, secondary pore structure and volume – of the treated samples strongly depend on the Si/Ti ratio of the parent TS-1 sample and the TPAOH concentration. For instance, high TPAOH concentration is necessary to induce titanium re-insertion into framework position and

to create inter-connected open meso/macropore in TS-1 with low Si/Ti ratio. On the contrary, TPAOH treatment even at high concentration was found to be ineffective in the post-synthesis treatment of low titanium containing TS-1 samples and result in a phase change from orthorhombic to monoclinic. The post-treated high titanium containing and inter-connected secondary pore TS-1 samples exhibited higher activity for cyclohexene epoxidation than the parent TS-1 sample with similar Si/Ti. This technique provides a controlled way of mesopore creation in TS-1 materials, which may be extended to other titanium base microporous materials.

KEYWORDS: Hollow TS-1, framework titanium, extra-framework titanium, dissolution, recrystallization process, tetrapropylammonium hydroxide

1 Introduction

Titanium silicalite-1 (TS-1) is a micro-porous, crystalline material with an MFI topology and is well-known as an excellent selective oxidation catalyst under mild conditions[1]. The hydrophobic environment of the titanium in TS-1 allows for their application with water-based peroxides. With aqueous H_2O_2 as the oxidant, TS-1 has been widely used in phenol hydroxylation[2], epoxidation of propylene[3] and cyclohexanone ammoximation[4] reactions. Although TS-1 exhibits good activity in the oxidation of many organic compounds, their micropore size is about 0.55 nm, which implies reactants with a larger molecular size cannot penetrate the TS-1 channels and are restricted to interact only with the active sites on their external surface or at pore mouth.

In order to enhance the accessibility of active centres by reacting molecules, hierarchical TS-1 with well-developed secondary porosity has been synthesized by various techniques including desilication[5], silanization[6], dissolution–recrystallization[2], dry gel conversion[7], soft templating[8] and hard templating[9, 10]. Among the variety of strategies in the preparation of hierarchical zeolites, dissolution-recrystallization method is well used in industrial applications[2], as treatment with TPAOH can create voids in TS-1 crystals and reinsert some extra framework titanium into framework position[2]. It is accepted that several types of titanium species can co-exist in TS-1 – the isolated titanium species in the framework, and the extra framework Ti species. It is commonly believed that the isolated titanium species in the framework of the TS-1 is the active centre for selective oxidation reactions, while the extra framework Ti species can lead to undesired decomposition of H_2O_2 [11]. Although the dissolution-recrystallization method has become a standard method to produce hollow TS-1 on an industrial scale [3, 4], the full potential of this technique is yet to be realised as the hollow TS-1 crystals often contain extra framework titanium species. Furthermore, the hollow pores created by this technique are generally closed secondary pore in the crystals, which hinders their usage for bulky molecular applications [3].

Previously, we treated a TS-1 material (Si/Ti of 46) with different TPAOH concentrations and we found that with a TPAOH concentration of greater than 0.4M the extra-framework Ti could be effectively converted into framework Ti, and the TPAOH concentration influenced the pore structure significantly. At low TPAOH concentration (i.e. less than 0.4 M), only closed meso-/macropores (grooves and

hollow cavities) can be created in the TS-1 crystals, whereas at an optimum concentration of 0.5 M TPAOH, open and connected hierarchical mesopores and macropores were created in the recovered TS-1. Such material with open and interconnected mesopores and macropores exhibited higher conversion during cyclohexene epoxidation compared to the sample with closed voids present in the crystals [12].

Recently, using similar approach to that of the TS-1 a method was developed to convert parent MFI zeolites ($\text{Si/Al} = 12$) with tetrahedral extra-framework Al into Al-enriched mesoporous ZSM-5 nanoboxes with low silicon-to-aluminium ratios ($\text{Si/Al} = 16$) [13]. The resulting hollow ZSM-5 zeolite with low Si/Al ratio exhibited excellent catalytic performance in hydrocarbon cracking, especially in the cracking of bulky molecules, with high activity, stability and selectivity to propylene [13]. These findings imply a careful control of the dissolution–recrystallization process can produce a better catalyst. To the best of our knowledge there are no systematic studies of factors that may influence the dissolution-recrystallization process.

In the present study, we employed three different TS-1 samples with different Si/Ti – 173, 102 and 30 – ratios to elucidate the influence of elemental composition and TPAOH concentration on the textural properties, crystal structure and positions of Ti species. These results are then compared to that in our previous work to give a systematic conclusion about the influence of Si/Ti ratio and TPAOH concentration on the textural properties and titanium position on TPAOH post-treated TS-1 materials.

2 Materials and Experimental Section

2.1 Materials

Tetraethyl orthosilicate (TEOS, Research Grade, 98%) and titanium (IV) ethoxide (TEOT, Technical Grade) used as the silica and titanium sources respectively.

Tetrapropyl ammonium hydroxide (TPAOH, 25wt% in H₂O) was used as the structure directing agent. All chemicals were sourced commercially from Sigma-Aldrich and used as received without further purification.

2.2 Synthesis of the parent TS-1

Titanium (IV) ethoxide (TEOT) (0.37 g for Si/Ti = 200, 0.75 g for Si/Ti = 100 and 2.08 g for Si/Ti = 25) was dissolved in Tetraethyl orthosilicate (TEOS) (67.7 g), then the mixture of 48.8 g TPAOH (40 wt %) and 82 g H₂O was added to the above mixture drop by drop. Mixtures of the following molar compositions (SiO₂:0.3 TPAOH:19 H₂O:wTiO₂, where w is 0.005, 0.01 and 0.029 for solid sample Si/Ti ratio of 173, 102 and 30 respectively) were hydrolysed with vigorous stirring for 4 hours at room temperature, then heated to 313 K under continuous stirring for 2 hours to remove alcohol and to obtain the synthesis gel. The solutions were transferred into Teflon-lined autoclaves, and hydrothermal reactions were performed at 433 K for 2 days. After the hydrothermal reaction, the autoclave was cooled to room temperature and the solid products were retrieved by centrifugation, then re-dispersed in water followed by centrifugation until the pH was approximately 7. The final solid product was dried at 110 °C overnight. To remove the structure directing agent, all samples were calcined in static air at 550 °C with a ramp rate of 1 °C min⁻¹ and held for 6 hours.

The samples with Si/Ti = 173, 102 and 30 were denoted as TT_173, TT_102 and TT_30, respectively.

2.3 Post-synthesis treatment

Approximately 2g of each sample were dispersed in 20 mL TPAOH solution of different concentration ($0.1\text{--}0.5\text{ mol L}^{-1}$) and stirred at 400 rpm for 20 minutes to form a slurry. The slurry obtained were placed in Teflon-lined autoclaves and hydrothermally treated at 160°C for 24 hours, after which the autoclaves were cooled to room temperature and the solid products were retrieved via centrifugation. The pH of the samples was lower to near 7 by dispersing in water and centrifuging followed by drying and calcination according to the same procedure and conditions in section 2.2. As an example of the sample notation, sample TT_173 treated with 0.1M TPAOH were denoted as TT_173_0.1M.

2.4 Characterisation Techniques

The phase purity and crystallinity of the synthesized materials were evaluated using the powder X-ray diffraction technique. The powder X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert Pro system fitted with a $\text{CuK}\alpha 1$ X-ray source operated at 40 kV and 40 mA. The relative crystallinity was calculated by comparing the total intensity of the five characteristic peaks of the XRD pattern from 22.5° to 24.6° with that of the pristine TS-1 sample[14].

The diffuse reflectance UV-vis spectra were recorded on a Hitachi U-3900H UV visible spectrophotometer, while infrared (FTIR) measurements was conducted on a

Nicolet NEXUS 670 FT-IR spectrometer to obtain details about the coordination state of titanium in the synthesised TS-1 samples.

Morphological characteristics of the samples were obtained using a Scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM images were recorded on an Inspect F50 at 20 KV while the TEM images were collected on a FEI Tecnai F20 S/TEM at 200 KV .

Textural properties (surface area and pore size analyser) were derived from the nitrogen adsorption-desorption isotherms measured at liquid nitrogen temperature (77 K) on a Micromeritics 3flex. Samples were outgassed at 623 K for 12 h, and textural properties were derived from the isotherms using the BET and t-plot method.

The Si/Ti ratio was determined by the ICP-AES technique. Prior to the ICP-AES analysis 0.1g of each TS-1 sample was dissolved in a 5 mL solution of 10 wt% hydrofluoric acid (HF) solution at RT, which was subsequently diluted to 100 mL with deionised water.

2.5 Catalytic Testing

As the molecular size of cyclohexene is larger than the pore size of TS-1 the catalytic activities of the prepared samples were evaluated towards cyclohexene epoxidation to illustrate the influences of the hierarchical porosity.

Typically, 0.1 g sample was dispersed in a reaction mixture consisting of 6 mmol of cyclohexene, 6 mmol of hydrogen peroxide (H_2O_2 , 30wt% in water), and 10 mL of acetonitrile (solvent) in a colaver glass reactor. The reactor was sealed, and the mixture was heated to 60 °C under stirring. The reaction was allowed to proceed for 4

hours, cooled to room temperature in an ice bath and the products were analysed by a gas chromatograph (Agilent 7890B) equipped with a flame ionization detector (FID) and Agilent CP7658I CP-Wax 52 CB column with dimensions of 25 m \times 0.53 mm \times 2 μ m. The carbon balance is above 95%.

3 Results and Discussions

3.1 Structural Analysis of the Samples

Figure 1 shows the X-ray powder diffraction patterns of as-prepared samples and the samples treated with different TPAOH concentrations in the 22° to 25° 2 θ range (please see Fig. S1 for the full range XRD patterns). Typically, a single peak at 2 θ diffraction angle of 24.3° for MFI type framework indicates an orthorhombic structure of unit cell symmetry, which is characteristic of substituted framework metal, whereas, a doublet at the same position is characteristic of a monoclinic unit cell symmetry for silicalite-1[13, 15]. The XRD patterns of TT_30 series samples shown in Fig. 1a, exhibit only a single peak at ca. 24.3° before and after treatment in TPAOH solution, which implies that they are of an orthorhombic unit cell. This observation implies that the TT_30 series samples retained their original TS-1 crystal structure, which is similar to our observation for the TS-1 with a Si/Ti ratio of 46 treated with different concentration of TPAOH solution reported in our previous work[12]. However, for the TT_102 series samples, the single peak at ca. 24.3° split into two peaks when the TPAOH concentration is higher than 0.1 M, which suggests a change from orthorhombic to monoclinic crystal phase (Fig. 1b). For TT_173 series samples, even at low TPAOH concentration of 0.1 M, the single peak at ca. 24.3° split into two peaks

(Fig. 1c). These results suggest that TS-1 with low titanium content is prone to loss of their titanium content during TPAOH treatment even at low concentration. Hence, it can be inferred that the higher the titanium content the more stable is the phase.

In addition to the TPAOH concentration, the relative crystallinity of the treated sample is also influenced by the titanium composition of the pristine sample. From Fig.1d, it is clear to see that the relative crystallinity increased first, then decreased with the increasing TPAOH concentration for TT_30 and TT_102 series samples. However, for the TT_173 series samples, the relative crystallinity monotonically decreased with the increasing TPAOH concentration. That means that the Si/Ti ratio and TPAOH concentration influenced the dissolution and recrystallization behaviour. The sample with low Si/Ti ratio lower than 46 can adjust to the process of dissolution and recrystallization[12] while the sample with a Si/Ti ratio higher than 102, TPAOH treatment degrades the structure of the TS-1 crystal and changes the crystal structure from orthorhombic to monoclinic, and transforms a limited amount of framework titanium to extra-framework.

3.2 Spectroscopic analysis

FTIR and diffuse reflectance UV-vis were used to evaluate the nature of the titanium species on both the original and the TPAOH treated samples. As shown in Fig S2, all the samples before and after TPAOH treatment retain the band at 960 cm^{-1} , which is attributable to titanium in the framework position[16]. Since the existence of extra framework species cannot be detected with the FTIR, we use the diffuse reflectance UV-vis (DRUV-Vis) spectroscopy to probe the presence of any extra-framework titanium in both the as-prepared and TPAOH treated samples, and to

monitor the role of the post-treatment conditions on the titanium distribution (Fig. 2). The peak ca. 210 nm in TS-1 is characteristic of isolated framework titanium species, while the peak at ca. 300 nm corresponds to extra framework titanium[17]. For the TT_30 series samples, the extra framework titanium first increased at low TPAOH concentration, however, as the concentration of the TPAOH increases the extra-framework titanium decreases (Fig. 2a). At Si/Ti ratio of 102 and 173 (Fig. 2b and 2c), TPAOH treatment leads to an increase in the extra framework titanium irrespective of the TPAOH concentration utilized, which may imply that de-metalation is the predominant process in this samples. Compared with the TS-1 with Si/Ti ratio of 46[12], it appears that the Si/Ti ratio influences the effective reinsertion of extra framework titanium into framework positions by this method.

Peak deconvolutions were performed on the DRUV-Vis spectra in figure 2 using the PeakFit program with the Gaussian fitting method[18] in order to quantify the amount of framework titanium in each sample, which is shown in figure 2d and Table S1. For TT_30 series samples, the content of framework titanium restored to the level of original sample after treatment with 0.4 M TPAOH. However, for TT_102 and TT_173 series samples, the framework titanium content was reduced from 100% to approximately 70%. From the above results, it is interesting to note that the amount of framework titanium is consistent with the crystal phase changes observed in figure 1. Comparing our previous results[12] with that of a sample with an Si/Ti ratio of 46, it appears that when the Si/Ti ratio is in the range of 46 and lower, TPAOH treatment does not affect the crystal phase, and the extra framework titanium in the original sample can be re-inserted into the framework at an optimum concentration of TPAOH.

However, when the Si/Ti ratio is higher than 102, TPAOH treatment changes the crystal phase of TS-1 from orthorhombic to monoclinic. In addition, at such high Si/Ti ratio it is expected that the titanium is well dispersed and well incorporated into the framework position and TPAOH treatment of such samples leads to the change of the framework titanium to extra framework titanium – probably by means of demetallation.

3.3 Textural Properties

The adsorption/desorption isotherms of the as-prepared and TPAOH treated samples are shown in Figure 3. All the original samples exhibit characteristic type I isotherms, which confirms their microporous nature independent of the framework Si/Ti ratio. The textural properties in Table 1 indeed confirm that the micropores are responsible for most of the surface area of the pristine samples with very little contribution by the mesopores. The TPAOH treated samples exhibited a combined type I and IV isotherm, which is characteristic of a hierarchical porous system with a combined micro- and mesoporosity. The Si/Ti ratio of the TPAOH treated TS-1 samples showed a marked influence on the hysteresis loop, which increases with decreasing Si/Ti ratio. Similarly, by increasing the TPAOH concentration, the size of the hysteresis loop also increases. These observations show that the mesoporous properties of the treated samples are influenced by the Si/Ti ratio of the materials and the concentration of the applied TPAOH. It can be seen from Table 1 and Figure 3d, that the development of mesoporosity is most significant in the low Si/Ti ratio of 30, exhibiting an increase in mesopore surface area in TT_30_0.4M of $194 \text{ m}^2\text{g}^{-1}$, while its isotherm shows a distinct hysteresis loop in the relative pressure range of 0.4–0.8, indicating a substantial amount of mesopores centered around 10 nm[2].

At a higher Si/Ti ratio of 102, the increase in mesopore surface area of $87 \text{ m}^2\text{g}^{-1}$ is significant but much lower than in the low Si/Ti range. The TT_173 series samples are modestly influenced by the TPAOH treatment as can be concluded from the similar isotherms of the TPAOH-treated samples and the un-treated pristine material (Figure 3c). The substantial mesopore formation upon TPAOH treatment does not decrease micropore volume for TT_30 and TT_102 or for the sample with Si/Ti ratio of 46 in our previous work but induces a decrease in micropore volume up to 20% for the sample with Si/Ti ratio of 173.

3.4 Morphological Characterisation

The SEM images of the as-prepared and TPAOH modified samples are shown in Fig. S3-S5. There are no obvious differences between the as-prepared (AP) sample and the TPAOH modified samples for the samples with Si/Ti ratio of 30 and 102. However, for the sample with Si/Ti ratio of 173, cracks and deformation can be seen in some crystals as the TPAOH concentration was increased to 0.5M. For all these samples – before and after TPAOH treatment – the crystal size remains similar without any obvious change. The silicon to titanium ratio of the samples evaluated by EDS before and after TPAOH treatment is given in table 1.

In order to get a direct observation of the changes in pore structure upon TPAOH treatment, all the samples were subjected to HRTEM analysis. HRTEM images of TT_30 series samples with different magnification are given in Figure 4. For the samples TT_30_0.1M, mesopores can be observed penetrating from the centre to the outer edge of the crystal (Figure 4a and b). When the TPAOH concentration is higher

than 0.2 M, the channel extends beyond the edges to the outside of the crystal, and a secondary channel is formed around the large channel (Figure 4c to f).

From the HAADF morphology of TT_30_0.4M (Figure 5a), it is obvious to see that the mesopore in the TS-1 is connected to the outer surface of the crystals, which is consistent with the results in our previous work[12], – open inter-connected pores can be created at TPAOH concentration of 0.4M to 0.5M in TS-1 crystals with Si/Ti ratio of 46. The presence of a homogeneous distribution of titanium in the TT_30_0.4M samples is clearly evidenced by the TEM-EDS mapping image of the crystal as given in Figure 5. Unlike the TS-1 samples with low Si/Ti ratio (TT_30), on which open mesopores could be induced, only closed mesopore could be induced on TT_102 and TT_173 with high Si/Ti ratio (Figure 6a-f). From the HAADF image of TT_102_0.5M and TT_173_0.5M (Fig. S6), it is more obvious that the mesopore in the crystals is not regular, with only a few of the mesopores connected to the external surface for TT_102_0.5M, while most of the mesopores are closed in the crystal for TT_173_0.5M.

3.5 Catalysis

The influence of the titanium distribution and the induced hierarchical porosity of the treated samples were evaluated with cyclohexene epoxidation. Table 2 shows the results of the catalytic activity and the product distribution over each sample. The three samples exhibited different catalytic performances.

The sample with Si/Ti ratio of 30 exhibited an increase in cyclohexene conversion with TPAOH concentration. A maximum of 28% conversion was reached in 4 hours over the 0.4M TPAOH sample, which corresponds to the highest level of connected and open mesopores in the sample. For the samples with higher ratio of

Si/Ti, there was no significant improvement in the conversion of cyclohexene until the TPAOH concentration has reached 0.5M, an indication that there was very little mesopores created prior to 0.5M. A maximum of 15% and 11% conversion in 4 hour was attained for both TT_102 and TT_173 respectively.

For TT_30 series samples, compared with the as-prepared sample, the TPAOH modified samples have a comparable selectivity to cyclohexene oxide, while the TPAOH modified samples have higher selectivity of 1,2-cyclohexanediol and lower selectivity of cyclohexen-1-one and 2-cyclohexen-1-ol an indication of less defect on the samples and reduced extra-framework titanium species in the treated samples. Unlike the TT_30 samples, the TT_173 series samples exhibited the opposite trend. With the increasing of TPAOH concentration, the selectivity of cyclohexene oxide and 1,2-cyclohexanediol decreased and the selectivity of cyclohexen-1-one and 2-cyclohexen-1-ol increased, which confirms the result of Figure 2 where extra-framework increased with TPAOH treatment. TT_102 series samples exhibited an intermediate behaviour compared to TT_30 and TT_173 series sample, the selectivity of cyclohexene oxide, 1,2-cyclohexanediol and cyclohexen-1-one and 2-cyclohexen-1-ol remained stable regardless of the concentration of TPAOH.

It is facile to create open secondary pores in the low Si/Ti ratio TS-1 with hydrothermal post-treatment with TPAOH, and the dissolved framework titanium can be reinserted into the framework, thereby promoting the conversion of cyclohexene and the formation of cyclohexene oxide, lowering the selectivity of by-products. On the contrary, only closed mesopores can be created in low Si/Ti ratio TS-1 by the same

technique, where the content of framework titanium is greatly reduced, resulting in low cyclohexene conversion and low selectivity to cyclohexene oxide.

4 Conclusions

In this report, we intended to gain a comprehensive understanding of the main factors that influence the creation of mesoporosity in TS-1 by a post-treatment method with TPAOH. Three kinds of TS-1 samples with a product Si/Ti ratio of 30, 102 and 173 were hydrothermally treated with different concentrations of TPAOH solution. It was found that the Si/Ti ratio of TS-1 and the concentration of TPAOH affect the mesopore volume, structure and the position of titanium species.

This technique seems to be more suitable for inducing open and connected mesopores in TS-1 with high titanium content, while at best closed mesopores are created in TS-1 with low titanium contents. Similarly, at high titanium content, extra-framework titanium in the sample can be successfully repositioned into the framework sites, whereas those samples with low titanium concentrations results in demetallation leading to extra-framework titanium in such samples

Acknowledgement

YJ gratefully acknowledge financial support from the Natural Science Foundation of Liaoning Province for his research (20180510012) and the China Scholarship Council (CSC) for his visiting fellowship in the UK (201604910181).

References

- [1] E. Duprey, P. Beaunier, M.A. Springuel-Huet, F. Bozon-Verduraz, J. Fraissard, J.M. Manoli, J.M. Brégeault, Characterization of Catalysts Based on Titanium Silicalite, TS-1, by Physicochemical Techniques, *Journal of Catalysis*, 165 (1997) 22-32.
- [2] Y. Wang, M. Lin, A. Tuel, Hollow TS-1 crystals formed via a dissolution–recrystallization process, *Microporous and Mesoporous Materials*, 102 (2007) 80-85.
- [3] M. Lin, C. Xia, B. Zhu, H. Li, X. Shu, Green and efficient epoxidation of propylene with hydrogen peroxide (HPPO process) catalyzed by hollow TS-1 zeolite: A 1.0kt/a pilot-scale study, *Chemical Engineering Journal*, 295 (2016) 370-375.
- [4] A. Zheng, C. Xia, Y. Xiang, M. Xin, B. Zhu, M. Lin, G. Xu, X. Shu, Titanium species in deactivated HTS-1 zeolite from industrial cyclohexanone ammoxidation process, *Catalysis Communications*, 45 (2014) 34-38.
- [5] A. Silvestre-Albero, A. Grau-Atienza, E. Serrano, J. García-Martínez, J. Silvestre-Albero, Desilication of TS-1 zeolite for the oxidation of bulky molecules, *Catalysis Communications*, 44 (2014) 35-39.
- [6] D.P. Serrano, R. Sanz, P. Pizarro, A. Peral, I. Moreno, Improvement of the hierarchical TS-1 properties by silanization of protozeolitic units in presence of alcohols, *Microporous and Mesoporous Materials*, 166 (2013) 59-66.
- [7] M. Wu, X. Liu, Y. Wang, Y. Guo, Y. Guo, G. Lu, Synthesis and catalytic ammoxidation performance of hierarchical TS-1 prepared by steam-assisted dry gel conversion method: the effect of TPAOH amount, *Journal of Materials Science*, 49 (2014) 4341-4348.
- [8] S. Du, Q. Sun, N. Wang, X. Chen, M. Jia, J. Yu, Synthesis of hierarchical TS-1 zeolites with abundant and uniform intracrystalline mesopores and their highly efficient catalytic performance for oxidation desulfurization, *Journal of Materials Chemistry A*, 5 (2017) 7992-7998.

- [9] W. Wang, G. Li, W. Li, L. Liu, Synthesis of hierarchical TS-1 by caramel templating, *Chemical Communications*, 47 (2011) 3529-3531.
- [10] A.-L. Adedigba, G. Sankar, C.R.A. Catlow, Y. Du, S. Xi, A. Borgna, On the synthesis and performance of hierarchical nanoporous TS-1 catalysts, *Microporous and Mesoporous Materials*, 244 (2017) 83-92.
- [11] G. Xiong, Y. Cao, Z. Guo, Q. Jia, F. Tian, L. Liu, The roles of different titanium species in TS-1 zeolite in propylene epoxidation studied by in situ UV Raman spectroscopy, *Physical Chemistry Chemical Physics*, 18 (2016) 190-196.
- [12] Y. Jiao, A.-L. Adedigba, Q. He, P. Miedziak, G. Brett, N.F. Dummer, M. Perdjon, J. Liu, G.J. Hutchings, Inter-connected and open pore hierarchical TS-1 with controlled framework titanium for catalytic cyclohexene epoxidation, *Catalysis Science & Technology*, 8 (2018) 2211-2217.
- [13] Y. Jiao, L. Forster, S. Xu, H. Chen, J. Han, X. Liu, Y. Zhou, J. Liu, J. Zhang, J. Yu, C. D'Agostino, X. Fan, Creation of Al-Enriched Mesoporous ZSM-5 Nanoboxes with High Catalytic Activity: Converting Tetrahedral Extra-Framework Al into Framework Sites by Post Treatment, *Angew Chem Int Ed Engl*, (2020).
- [14] W. Song, G. Xiong, H. Long, F. Jin, L. Liu, X. Wang, Effect of treatment with different bases on the catalytic properties of TS-1/SiO₂ extrudates in propylene epoxidation, *Microporous and Mesoporous Materials*, 212 (2015) 48-55.
- [15] Y. Jiao, X. Fan, M. Perdjon, Z. Yang, J. Zhang, Vapor-phase transport (VPT) modification of ZSM-5/SiC foam catalyst using TPAOH vapor to improve the methanol-to-propylene (MTP) reaction, *Applied Catalysis A: General*, 545 (2017) 104-112.
- [16] B. Wang, X. Peng, W. Zhang, M. Lin, B. Zhu, W. Liao, X. Guo, X. Shu, Hierarchical TS-1 synthesized via the dissolution-recrystallization process: Influence of ammonium salts, *Catalysis Communications*, 101 (2017) 26-30.

- [17] C. Liu, J. Huang, D. Sun, Y. Zhou, X. Jing, M. Du, H. Wang, Q. Li, Anatase type extra-framework titanium in TS-1: A vital factor influencing the catalytic activity toward styrene epoxidation, *Applied Catalysis A: General*, 459 (2013) 1-7.
- [18] Y. Zuo, M. Liu, T. Zhang, L. Hong, X. Guo, C. Song, Y. Chen, P. Zhu, C. Jaye, D. Fischer, Role of pentahedrally coordinated titanium in titanium silicalite-1 in propene epoxidation, *RSC Advances*, 5 (2015) 17897-17904.

Table1: Summary of the textural properties As-prepared and TPAOH modified TS-1($V_{\text{meso}} = V_t - V_{\text{micro}}$)

Sample	S_{BET} [m ² g ⁻¹]	S_{micro} [m ² g ⁻¹]	S_{BJH} [m ² g ⁻¹]	V_{micro} [cm ³ g ⁻¹]	V_{meso}^a [cm ³ g ⁻¹]	V_t [cm ³ g ⁻¹]	Si/Ti [mol/mol]
TS_30	478	450	28	0.153	0.077	0.230	30
TS_30_0.1M	522	437	86	0.176	0.105	0.281	27
TS_30_0.2M	521	357	165	0.166	0.151	0.317	26
TS_30_0.3M	530	355	175	0.169	0.166	0.335	27
TS_30_0.4M	547	353	194	0.165	0.194	0.359	26
TS_102	494	482	13	0.170	0.049	0.219	102
TS_102_0.1M	469	437	33	0.160	0.061	0.221	91
TS_102_0.2M	414	345	69	0.166	0.077	0.243	76
TS_102_0.3M	435	360	75	0.168	0.091	0.259	71
TS_102_0.4M	416	331	85	0.167	0.082	0.249	75
TS_102_0.5M	405	319	87	0.168	0.107	0.275	82
TS_173	454	437	17	0.169	0.05	0.219	173
TS_173_0.1M	389	355	34	0.134	0.082	0.216	163
TS_173_0.2M	387	343	45	0.135	0.09	0.225	154
TS_173_0.3M	423	381	43	0.131	0.12	0.251	140
TS_173_0.4M	399	354	45	0.129	0.121	0.250	149
TS_173_0.5M	396	338	59	0.135	0.127	0.262	149

Table 2: Cyclohexene conversion and product selectivity over the as-prepared and TPAOH treated samples (reaction conditions; cyclohexene: 6 mmol, H₂O₂ (30 wt% in water): 6 mmol, Acetonitrile: 10mL, temperature: 60°C, reaction time: 4 hours). Carbon balance was always above 95%. All catalysis data are within 3% error margin.

Sample	Cyclohexene conversion [%]	Selectivity [%]		
		Cyclohexene epoxide	1,2-cyclohexanediol	Cyclohexen-1-one & 2-cyclohexe-1-ol
TT_30	16.1	75.2	11.9	12.9
TT_30_0.1M	19.2	75.6	19.0	5.4
TT_30_0.2M	21.7	74.2	20.6	5.2
TT_30_0.3M	25.8	74.3	20.7	4.9
TT_30_0.4M	27.7	84.8	12.5	2.7
TT_102	8.3	67.8	2.4	29.7
TT_102_0.1M	7.8	58.6	25.4	16.0
TT_102_0.2M	5.8	62.1	25.0	12.9
TT_102_0.4M	6.1	61.4	24.8	13.8
TT_102_0.5M	14.7	60.8	26.9	12.3
TT_173	9.2	62.0	14.6	23.4
TT_173_0.1M	5.4	50.5	35.5	14.0
TT_173_0.2M	5.4	51.8	33.3	14.9
TT_173_0.3M	6.4	41.1	25.2	33.7
TT_173_0.5M	10.7	44.5	22.7	32.8

Figure captions

Figure 1 – X-ray powder diffraction patterns (22° to 25° 2θ) of (a) TT_30, (b) TT_102, (c) TT_173 series samples and (d) their relative crystallinity. [O and M denote orthorhombic and monoclinic phase respectively]

Figure 2 – UV-vis curves of TT_30 (a), TT_102 (b), TT_173 series samples (c) and framework titanium amount of the above samples (d)

Figure 3 – Nitrogen adsorption and desorption isotherms of TT_30 (a), TT_102 (b), TT_173 series (c) samples and external surface area for the above samples (d)

Figure 4 – HRTEM morphology of TT_30_0.1M (a, b), TT_30_0.2M (c, d) and TT_30_0.4M (e, f)

Figure 5 – HAADF morphology (a) and TEM-EDX (b, c, d) images of TT_30_0.4M, Orange, yellow and green colours represent oxygen, silicon and titanium, respectively

Figure 6 – HRTEM morphology of TT_102_0.1M (a), TT_102_0.2M (b), TT_102_0.5M (c), TT_173_0.1M (d), TT_173_0.2M (e) and TT_173_0.5M (f)

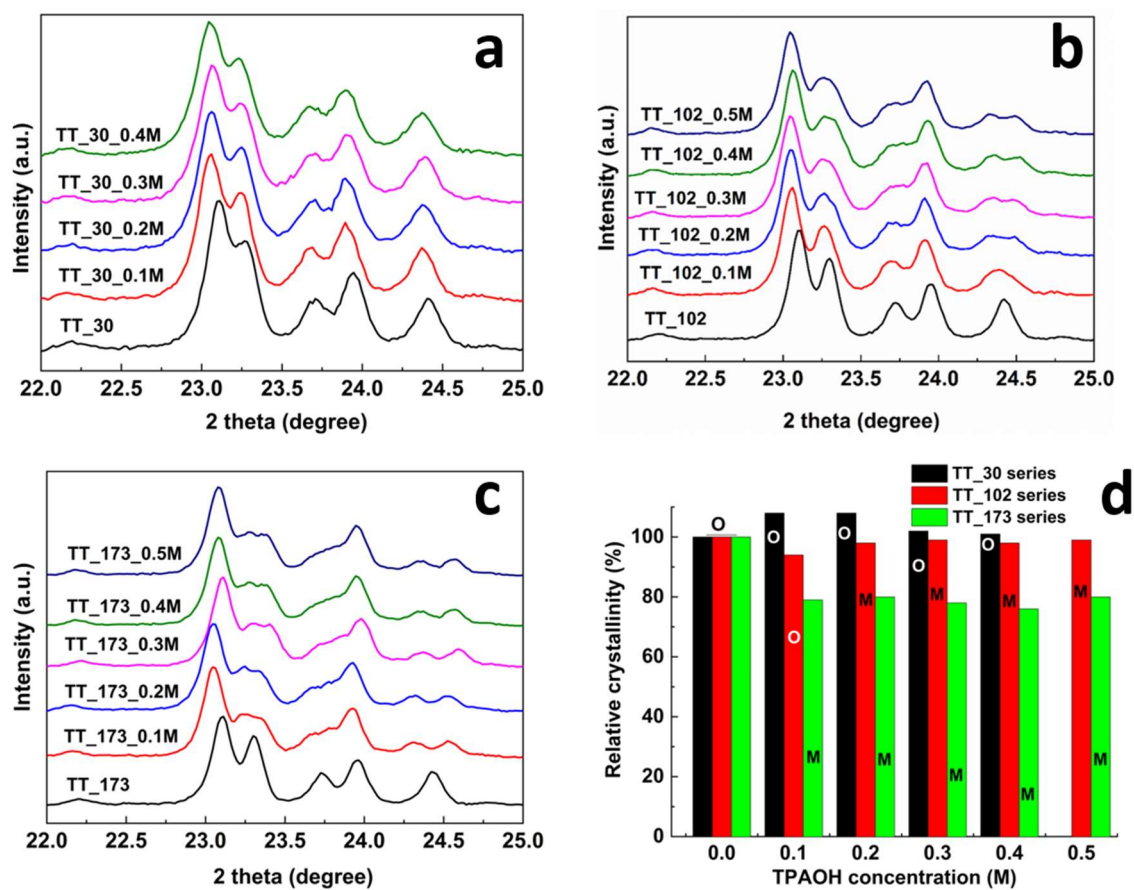


Figure 1: X-ray powder diffraction patterns (22° to 25° 2θ) of (a) TT_30, (b) TT_102, (c) TT_173 series samples and (d) their relative crystallinity. [O and M denote orthorhombic and monoclinic phase respectively)

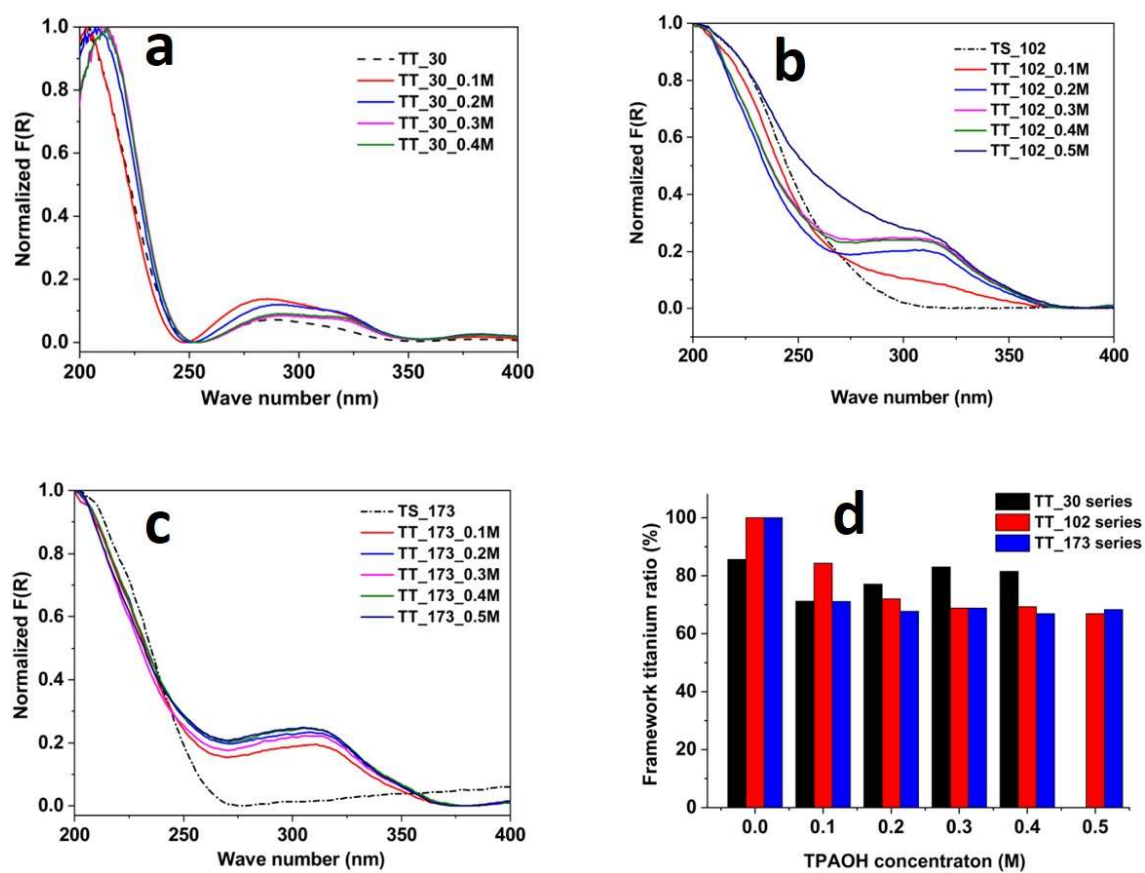


Figure 2: UV-vis curves of TT_30 (a), TT_102 (b), TT_173 series samples (c) and framework titanium amount of the above samples (d)

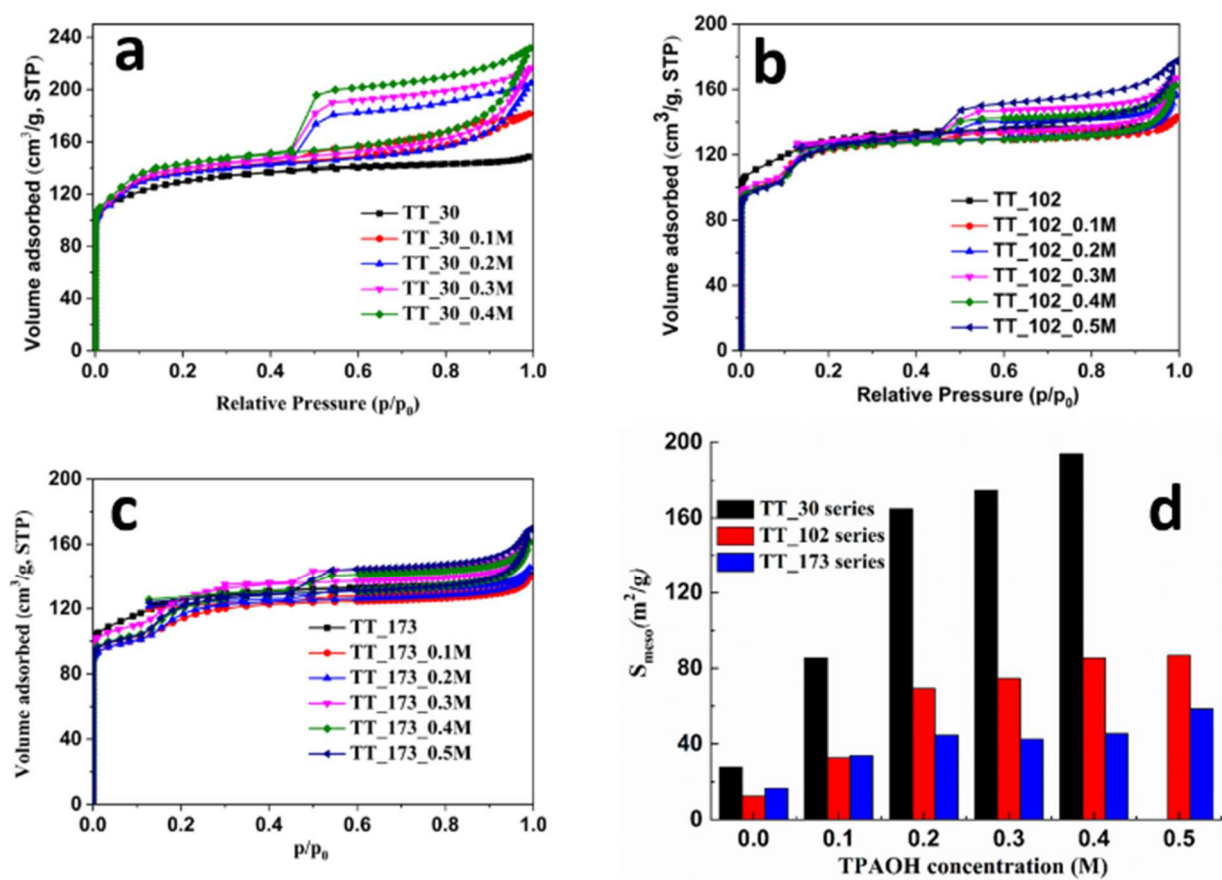


Figure 3: Nitrogen adsorption and desorption isotherms of TT_30 (a), TT_102 (b), TT_173 series (c) samples and external surface area for the above samples (d)

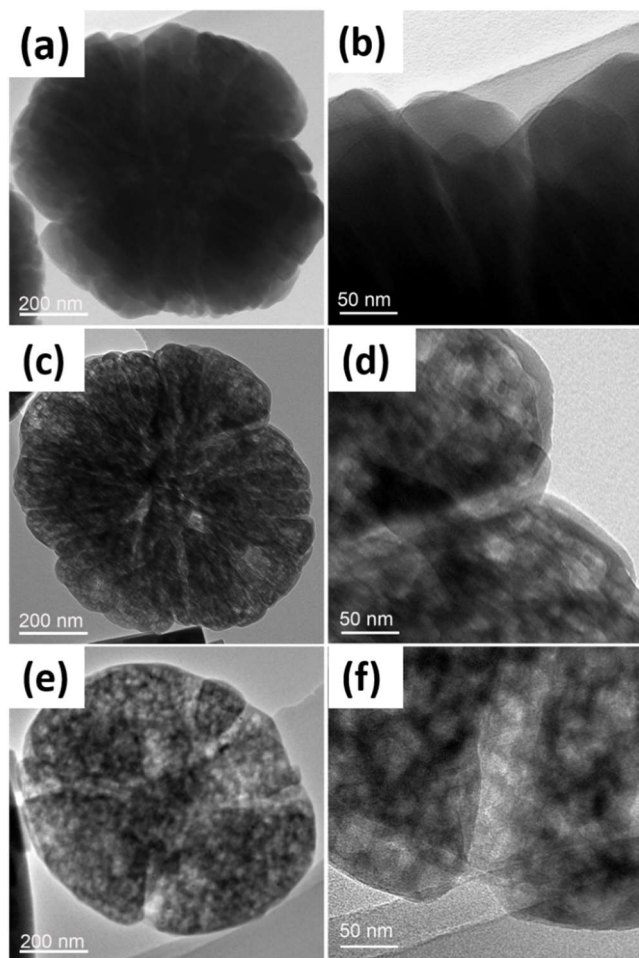


Figure 4: HRTEM morphology of TT_30_0.1M (a, b), TT_30_0.2M (c, d) and TT_30_0.4M (e, f)

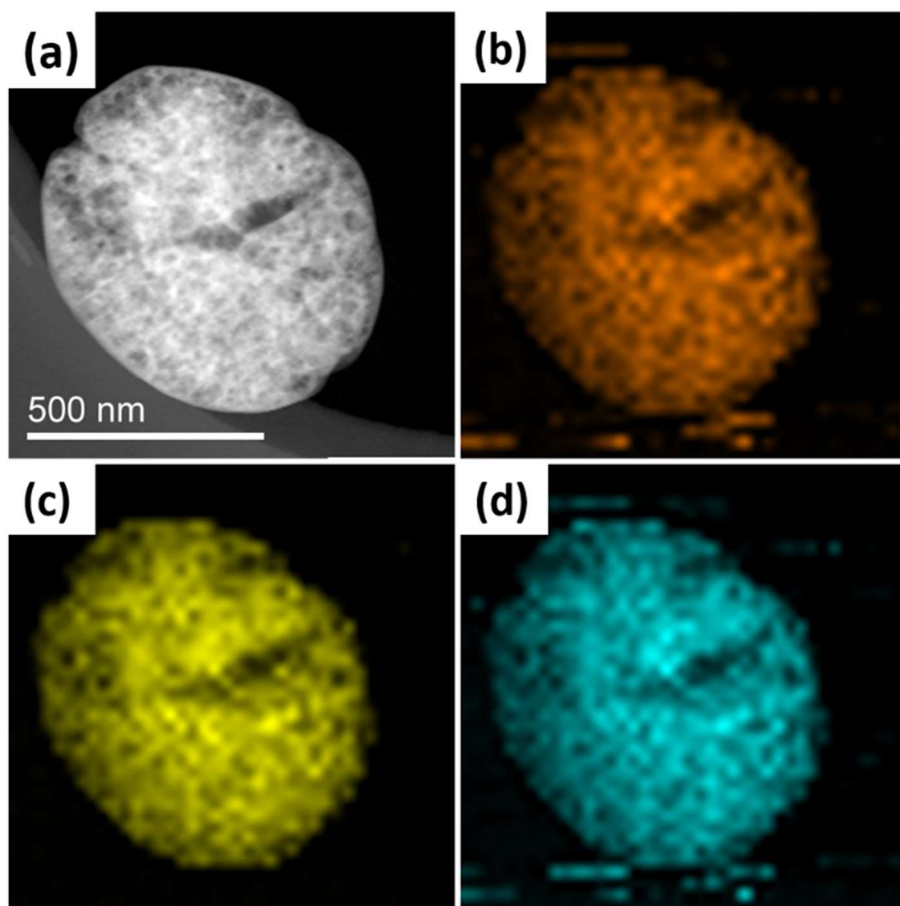


Figure 5: HAADF morphology (a) and TEM-EDX (b, c, d) images of TT_30_0.4M, Orange, yellow and green colours represent oxygen, silicon and titanium, respectively

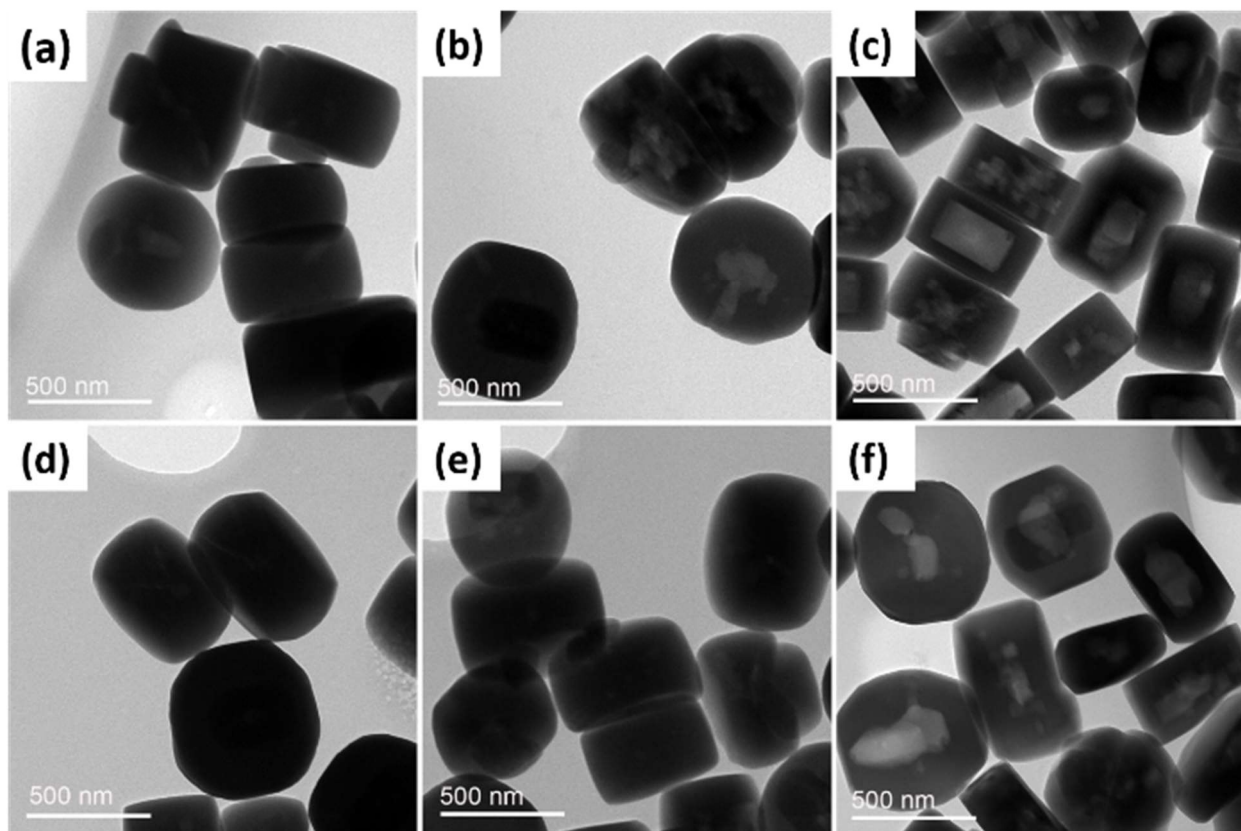


Figure 6: HRTEM morphology of TT_102_0.1M (a), TT_102_0.2M (b), TT_102_0.5M (c), TT_173_0.1M (d), TT_173_0.2M (e) and TT_173_0.5M (f)