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Intermediate-Crystallization Promoted Catalytic Activity of Titanosilicate Zeolites

Risheng Bai,^a Qiming Sun,^a Yue Song,^a Ning Wang,^a Tianjun Zhang,^a Fei Wang,^c Yongcun Zou,^a Zhaochi Feng,^b Shu Miao^b and Jihong Yu^{*a, d}

The exploration of highly efficient catalysts based on nano-sized hierarchical titanosilicate zeolites with controllable active titanium species is of great importance in promoting the oxidative desulfurization of bulky organosulfur compounds. Here we report the anatase-free nano-sized hierarchical TS-1 (**MFI**) zeolite prepared via the seed-assisted hydrothermal method. Interestingly, it is found that the intermediately crystallized zeolite phase exhibits better performance in oxidative desulfurization of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), with turnover number up to 17.9 and 18.0 at 30 min of the reaction, respectively, almost two folds higher than the final completely crystallized zeolite phase (8.8 and 6.7, respectively). This superior activity is attributed to the existence of abundant inter- and intracrystalline mesopores, the surface enriched active titanium species, as well as the absence of anatase species within nano-sized intermediate phase, which is beneficial for exposing more accessible active sites, enhancing the mass transfer efficiency, as well as avoiding the inefficient decomposition of oxidants. This intermediate crystallization method provides a useful strategy in exploring high-efficient zeolite catalysts.

Introduction

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Increasingly stringent regulations have been imposed worldwide to limit the content of sulfur compounds in liquid fuels to less than 10 ppm for the growing environmental problems.^{1, 2} Oxidative desulfurization (ODS)³ has proven to be an effective method in removing thiophenic compounds for the low investment and operating costs, mild operating conditions, as well as high desulfurization rate. Liquid acid,⁴ oxides,⁵ and polyoxometalates⁶ have been applied in the ODS process, however, these catalysts suffer from low oxidant utilization rate, poor stability or reusability, as well as the corrosion to equipment during catalyst preparation process or the catalytic reactions. Therefore, developing ODS catalysts with high reaction activity and excellent stability is of great importance.

Zeolites are microporous crystalline materials with welldefined pores and channels of molecular dimensions (< 2nm), which are widely used in ion-exchange, gas adsorptionseparation, and catalysis, and play an important role in

reactions, including selective oxidation of alkenes and alkanes, ammoximation of ketones, hydroxylation of phenol, and especially the deep oxidative desulfurization.¹¹⁻¹⁵ The ODS process over titanosilicate zeolite catalysts can be performed at a relative low temperature (60-90 °C) and atmosphere pressure. However, the conventional microporous TS-1 zeolite catalysts are less efficient in removing heterocyclic aromatic sulfur compounds such as dibenzothiophene (DBT) and 4,6dimethyldibenzothiophene (4,6-DMDBT), because of their steric hindrance arising from alky-groups that makes them inaccessible to the active sites located inside the zeolite. Recently, zeolites with extra-large pores, nanoscaled sizes, layered and hierarchical structures have been developed to overcome the limitation of the narrow channels of the traditional microporous zeolites; the highly accelerated mass transport, and sufficiently accessible active sites can remarkably improve the catalytic activity of reactions involving bulky molecules. $^{\rm 16\mathchar`-23}$ Up to now, various of hierarchical TS-1 zeolites have been synthesized by the utilization of strategies including: (i) templating strategies, such as hard templating and soft templating;²⁴ (ii) post-treatment strategies, such as steaming or acid treatment, desilicated, and chemical treatment.²⁵⁻²⁷ These prepared hierarchical titanosilicate zeolites show enhanced performance in the oxidative desulfurization reactions for bulky organosulfur compounds compared to the conventional microporous zeolites. However, the multi-step synthesis procedures, expensive cost of the additional mesoporogens, as well as the reduced crystallinity

sustainable chemistry.⁷⁻¹⁰ Titanosilicates, such as TS-1 (MFI)

zeolite, have been applied in many important catalytic

^{a.} State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University Changchun 130012, China

^{b.} State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

^c State Key Laboratory of Superhard Materials, Jilin University Changchun 130012, China

^d International Center of Future Science, Jilin University, Changchun 130012, China Electronic Supplementary Information (ESI) available: [Syntheses of the various titanosilicates. Details of the cata-lytic reactions. SEM images, TEM images, 29Si MAS NMR spectra, FT-IR spectra, XRD patterns, and UV-visible spectra of the prepared samples.]. See DOI: 10.1039/x0xx00000x

of zeolites remarkably limit the large-scale industrial applications of hierarchical TS-1 zeolites. Particularly, during the zeolite crystallization process, some anatase TiO₂ species are always formed inevitably, which cause the ineffective decomposition of oxidants and also cover active titanium sites.²⁸ Therefore, development of a simple and cost-effective synthetic strategy for highly efficient anatase-free hierarchical titanosilicate zeolite catalysts is full of challenge.

On the other hand, the titanium coordination states have influence on the catalytic activity of titanosilicate zeolites. It was reported that besides the tetra-coordinated titanium sites, the hexa-coordinated titanium species in titanosilicate zeolite catalysts are also responsible for the enhanced performance in alkene epoxidations.²⁹⁻³¹ Therefore it is important to construct active titanium species by tuning the titanium coordination states to improve the catalytic activity of titanosilicate zeolites.

Note that the completely crystallized zeolite catalysts are usually pursued for their good crystallinity, high surface area, and excellent hydrothermal stability. However, in the present work, we find that the intermediately crystallized nano-sized hierarchical TS-1 zeolite prepared via the seed-assisted hydrothermal method exhibits better performance in oxidative desulfurization of DBT and 4,6-DMDBT than the completely crystallized zeolite phase. The excellent catalytic activity is attributed to the easily accessible active sites and the enhanced mass transfer benefitted from abundant inter- and intracrystalline mesopores in nano-sized crystals, as well as the surface enriched active titanium species and the absence of anatase species in the intermediately crystallized catalysts. This discovery provides a useful guidance for the preparation of high-efficient zeolite catalysts utilized in catalytic reactions.

Experimental section

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Synthesis of nano-sized silicalite-1 zeolite seeds. The nanosized silicalite-1 zeolite seeds were synthesized with tetrapropylammonium hydroxide (TPAOH) as the organic structure directing agent with the molar composition of 1.0 SiO₂: 0.4 TPAOH: 30 H₂O. As a typical procedure: the organic template TPAOH was mixed with distilled water and stirred for 15 min, followed by the addition of tetraethylorthosilicate (TEOS). After a continuous stirring for 2 h, TEOS was fully hydrolyzed. Then the reaction mixture was transferred into a Teflon-lined stainless steel autoclave and then transferred into a pre-heated oven at 170 °C for 4 days under static conditions. The as-synthesized zeolites were washed thoroughly with water and ethanol, and then dried at 80 °C in the oven overnight, followed by calcination in air atmosphere at 550 °C for 6 h.

Synthesis of nano-sized hierarchical TS-1 zeolites. The nanosized hierarchical TS-1 zeolites were synthesized with the molar composition of 1.0 SiO₂: 0.025 TiO₂: 0.4 TPAOH: 50 H₂O: 10 wt% Seeds, under hydrothermal conditions at 170 °C with the crystallization time of 1-24 h, and the resulting products were named as TS-1(Hx), where x represented the crystallization time in hour. The zeolite samples crystallized for 1h, 3h, and 24h are denoted as TS-1(H1), TS-1(H3) and TS- 1(H24), respectively. Typically, the initial gel was prepared by mixing the TPAOH with distilled water, followed by the addition of TEOS and tetrabutyl titanate (TBOT), and then stirred for 2 h continuously. Finally, the seeds were added into the solution and stirred for another 2 h continuously. The resulting mixture was charged into autoclaves and crystallized in an oven at 170 °C for 1-24 h. The as-prepared zeolite products were washed thoroughly with water and ethanol, and then dried at 80 °C in the oven overnight, followed by calcination in air atmosphere at 550 °C for 6 h.

Synthesis of conventional nano-sized TS-1. Conventional nano-sized TS-1 zeolites were synthesized with the same molar composition of the TS-1(Hx) samples without adding zeolite seeds. The TS-1(con) sample was crystallized for 24 h, and some other samples named as TS-1(Cx) were crystallized for 2-12 h, where x represented the crystallization time in hour.

Catalytic tests. A certain amount of dibenzothiophene (DBT)/4,6-dimethyldibenzothiophene (4,6-DMDBT) was dissolved in n-octane to act as model fuel, and the concentration of sulfur in the model fuel was about 500 ppm. The reaction was performed in a 50 mL three neck glass flask with an oil bath under vigorous stirring (600 rap/min). In a standard run, 10 mL of model fuel and proper amount of catalyst were added to the reactor, with the molar ratio of reactant to titanium in zeolite catalysts was fixed at 10. The tert-butylhydroperoxide (TBHP) was used as oxidant, and the molar ratio of TBHP to the sulphide was 2. The reaction was carried at 60 °C for 30 min. Then, filtering the reacted solution and analyzing the TBHP conversion by titration with Ce(SO₄)₂ and Ferroin as the indicator. The products were analyzed by Gas chromatography-mass spectrometry (GC-MS, Thermo Fisher Trace ISQ, equipped with TG-5MS column, 60 m × 320 μ m × 25 μ m). Mass balances were accurate to within 5%.

Results and discussion

The nano-sized hierarchical zeolites (denoted as TS-1(H1), TS-1(H3) and TS-1(H24), and the 1, 3, and 24 represent for crystallization time in hour) were synthesized by introducing silicalite-1 zeolite seeds into the synthetic gel with the molar composition of 1.0 SiO₂: 0.025 TiO₂: 0.4 TPAOH: 50 H₂O: 10 wt% Seed under hydrothermal conditions. The product yields of the TS-1(H1), TS-1(H3), and TS-1(H24) are 8.4%, 75.9%, and 96.3%, respectively. Scanning electron microscope (SEM) and transmission electron microscopy (TEM) images show that the



Figure 1. (a) XRD patterns and (b) N_2 adsorption and desorption isotherms of the conventional nano-sized TS-1(con) and the nano-sized hierarchical TS-1(H1), TS-1(H3) and TS-1(H24) zeolite catalysts.

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Figure 2. TEM images and selected area electron diffraction patterns of nano-sized hierarchical TS-1(H1) (a-c), TS-1(H3) (d-f), and TS-1(H24) (g-i) zeolite catalysts. Scale bar, 20 nm.

silicalite-1 seeds have a hexagonal morphology with the size of around 250 nm (Figure S1). For comparison, conventional nano-sized TS-1 zeolites were also synthesized with the same molar composition of the TS-1(Hx) samples without adding zeolite seeds (Figure S2).

Powder X-ray diffraction (XRD) patterns of the prepared TS-1 zeolites show the typical diffraction peaks of the **MFI** structure, indicating the phase purity of the samples (Figure 1a and Table S2). SEM images reveal that all of these nano-sized hierarchical TS-1 zeolite samples crystallized for 1 h and 3 h are single particles with a regular ellipsoid morphology (100-250 nm), and the sample crystallized for 24 h (TS-1(H24)) as well as the conventional nano-sized TS-1 zeolite (TS-1(con)) exhibit a regular hexagonal morphology (150-300nm) (Figure S3).

Figure 2 and Figure S4 show the TEM images of the samples.TS-1(H1) consists of aggregated small crystals with dimensions of 5-10 nm. TS-1(H3) displays abundant intracrystalline mesopores, as well as the intercrystalline mesopores formed by the stacking of the TS-1 nanocrystals. The completely crystallized TS-1(H24) sample also shows abundant uniform intracrystalline mesopores. The selected area electron diffraction (SAED) patterns of TS-1(Hx) all show discrete spots indexed to the (002) and (020) planes of the **MFI** phase, indicating the single-crystalline nature of these prepared samples. The STEM-energy-dispersive X-ray spectrometry (EDX) analysis for the TS-1(H3) sample shows that the titanium atoms are distributed uniformly in the zeolite crystals (Figure S5).

As shown in Table 1, Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) gives the Si/Ti ratios 160.5, 83.6, and 77.8 for the TS-1(H1), TS-1(H3), and TS-1(H24), respectively, indicating that more titanium elements are incorporated into the crystals with the crystallization time prolonged. The Si/Ti ratios measured by X-ray photoelectron

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spectroscopy (XPS) are 119.2, 64.9. 75.8 for the three TS-1(Hx) samples, which are higher than the corresponding ICP results, indicating that the titanium species in the intermediately crystallized zeolites are much more surface enriched. ²⁹Si MAS NMR spectra of these TS-1(Hx) samples all give resonance bands mainly centered at -114 ppm (Figure S6), attributed to the tetrahedral framework silicon.³²

UV-Visible spectroscopy is utilized to investigate the coordination states of titanium in these samples. As shown in Figure 3a, the adsorption bands of TS-1(H1) and TS-1(H3) mainly appear at around 220 and 270 nm, which are attributed to the tetra-coordinated titanium³³ and hexa-coordinated titanium species, respectively. Note that the characteristic peak at about 330 nm for anatase species cannot be observed in these two samples. However, a strong absorption peak at about 330 nm can be obviously detected in TS-1(H24) sample, indicating the existence of anatase species. The conventional TS-1(con) zeolite shows the absence of hexa-coordinated titanium (270 nm) and the existence of the anatase species (330 nm). It is clear that by modulating the crystallization time, the formation of anatase species in the TS-1 samples can be avoided. The probable reason is that the extra-framework titanium can be stabilized as hexa-coordinated titanium species in the intermediately crystallized zeolite phase, while with the crystallization time prolonging, the surface titanium species may form the anatase species upon calcination.³⁴

Anatase TiO_2 is sensitive to the ultraviolet Raman resonance spectroscopy (UV-Raman) with the excitation wavelength of 320 nm.³⁵ The bands at 144, 390, 516, and 637 cm⁻¹ are attributed to the anatase TiO_2 .³⁶ As shown in Figure 3b, a strong band at 144 cm⁻¹ appears in the spectra of both the conventional nano-sized TS-1 and the TS-1(H24) samples, indicating the existence of anatase TiO_2 , but these characteristic peak of anatase TiO_2 is absent in both TS-1(H1) and TS-1(H3) samples. These results are in accordance with the UV-Vis spectroscopic analyses.

The Fourier-transform infrared spectroscopy (FT-IR) measurements are performed to investigate the state of titanium in the TS-1 samples. All the spectra show the adsorption peaks at 960 cm⁻¹ assigned to the stretching vibration of the Si–O bond with titanium atoms at coordination sites (Figure S7).³⁷

Nitrogen adsorption-desorption isotherms of nano-sized hierarchical TS-1(H1) sample shows a typical type-I isotherm as with conventional nano-sized TS-1, while the isotherms of the



Figure 3. UV-Vis spectra (a) and UV-Raman spectra (b) of conventional nano-sized TS-1(con) and TS-1(Hx) zeolite catalysts. The wavelength of the excitation light in UV-Raman is 320 nm.

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Scheme 1. Synthesis of the intermediately and completely crystallized zeolite catalysts



TS-1(H3) and TS-1(H24) samples give large hysteresis loops near saturation pressure ($0.8 < P/P_0 < 0.99$), arising from the aggregation of small crystallites and the existence of mesopores (Figure 1b).³¹ The nano-sized hierarchical samples TS-1(H1), TS-1(H3), and TS-1(H24) exhibit larger external surface areas (118-215 m²/g) and mesopore volumes (0.18- $0.23 \text{ cm}^3/\text{g}$) than those of traditional nano-sized TS-1 sample $(105 \text{ m}^2/\text{g} \text{ and } 0.11 \text{ cm}^3/\text{g})$. TS-1(H1) exhibits the highest BET surface area and the external surface area (464 m²/g, 215 m²/g), which may arise from the aggregated nano TS-1 crystals (5-10 nm). Besides, the high external surface area of TS-1(H3) $(149 \text{ m}^2/\text{g})$ ascribes to the ultra-small crystallites as well as the inter- and intracrystalline mesopores. As for the completely crystallized TS-1(H24), the microporous surface area increases to 295 m^2/g , and the external surface area decreases to 118 m²/g. The detailed surface area and pore volume data are summarized in Table S1. The density functional theory (DFT) pore size distributions of these prepared samples further demonstrate the existence of mesopores (Figure S8).

To investigate the formation process of the nano-sized hierarchical TS-1 crystals, the samples with different crystallization time are synthesized. According to the TEM measurements, we propose a possible crystallization process as shown in Scheme 1. After adding the nano zeolite seeds into the initial gel, the seeds are dissolved as silicalite-1 structural fragments in the gel.^{38, 39} At the beginning of the crystallization stage (Figure S9a), TS-1 zeolite crystals grow on the surface of the silicalite-1 structure fragments from the seed, forming nano TS-1 crystals of about 5-10 nm to give rise to the intercrystalline mesopores by aggregation. With the crystallization process continuing, the small nano crystals develop into a single nano crystal with both the inter- and intracrystalline hierarchical pores (Figure S9b-d). Finally, the intermediately crystallized zeolite crystal evolves into a wellcrystallized crystal with regular hexagonal morphology and abundant intracrystalline mesopores via ripening mechanism (Figure S9e-f). Note that the intermediately crystallized crystals, and completely crystallized crystals are all single crystals as proved by EM analyses (Figure 2).

It is believed that the zeolite seeds introduced into the synthesis gel not only play a crucial role in the formation of hierarchical structures, but also accelerate the crystallization processes and improve the crystallinity and yields of zeolite products. As shown in Figure S10, TEM images of the conventional nano-sized TS-1 zeolites synthesized without seeds clearly reveal that there are no intracrystalline mesopores in the crystals crystallized for 2-24 h. Besides, according to the XRD analyses, both the crystallinity and the yields of hierarchical TS-1 zeolites synthesized with seeds are higher than those of the counterpart synthesized without seeds (Figures S11-S12 and Tables S2-S3).

Oxidative desulfurization of dibenzothiophene (DBT) and 4,6- dimethyldibenzothiophene (4,6-DMDBT) are performed to



Table 1. Oxidative desulfurization of DBT and 4,6-DMDBT with TBHP as the oxidizing agent over Various Titanosilicate Catalysts.^a

Samples	Si/Ti ^b	Si/Ti ^c	Conv. (%)		Conv. (%)		TON ^g	TON ^h	Yield (%) ⁱ		Yield (%) ⁱ	
			DBT^{d}	4,6-DMDBT ^d	TBHP _{DBT} ^e	TBHP _{4,6-DMDBT} ^f	TON	TON	DBSO	DBSO ₂	DMDBSO	DMDBSO ₂
TS-1(H1)	160.5	119.2	100	100	91.7	92.9	18.0	18.1	18.8	81.2	17.9	82.1
TS-1-(H3)	83.6	64.9	100	100	90.8	91.6	17.9	18.0	19.4	80.6	19.1	80.9
TS-1(H24)	77.8	75.8	55.5	50.4	76.8	73.8	8.8	6.7	22.2	33.3	33.3	17.1
TS-1(C3)	97.3	86.6	60.7	53.8	56.4	58.9	7.1	6.1	50.3	10.4	46.5	7.3
TS-1(con)	73.2	79.4	27.3	17.7	33.4	30.2	3.1	1.8	23.6	3.7	16.4	1.3

^a Reaction conditions: 10mL 500 ppm model fuels, 60 °C, the molar ratio of n(sulphide)/n(Ti in zeolite) was fixed at 10, n(sulphide)/n(TBHP) was 0.5. ^b Measured by inductively coupled plasma (ICP). ^c Measured by X-ray photoelectron spectroscopy (XPS). ^d After 30 min of the catalytic reaction. ^e Conversion of TBHP in the oxidation of DBT, after 30 min of the reaction. ^f Conversion of TBHP in the oxidation of 4,6-DMDBT, after 30 min of the reaction. ^g Turnover number (moles of converted DMDBT and DMDBSO per mole of Ti site). ⁱ Product yield based on the DBT or 4,6-DMDBT after 30 min of the reaction.

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investigate the catalytic activity of nano-sized hierarchical zeolites with TBHP as the oxidizing agent (Table 1 and Figures (S13-S14). As compared with the conventional nano-sized TS-1(con) catalyst, all of the TS-1(Hx) catalysts show an outstanding performance in removing the bulky organosulfur compounds. Significantly, the intermediately crystallized TS-1(H3) catalyst exhibit the superior catalytic performance in oxidative desulfurization of DBT and 4,6-DMDBT, which can be completely converted in just 15 minutes, much higher than the completely well-crystallized zeolite catalyst TS-1(H24) (49.1% for DBT and 36.5% for 4,6-DMDBT at 15 min) as well as other reported hierarchical titanosilicate zeolites (Table S4).⁴⁰ Since Si/Ti ratios of the samples are different, the Turnover Number (TON) values were calculated to illustrate the intrinsic activity of the catalysts after 30 min of the reaction (Table 1). The intermediately crystallized TS-1(H3) gives the TON of DBT and 4,6-DMDBT up to 17.9 and 18.0, respectively, almost two folds higher than those of the completely well-crystallized zeolite TS-1(H24) (8.8 for DBT and 6.7 for 4,6-DMDBT). The fact that the intermediately crystallized TS-1 catalysts give higher selectivity toward the final product sulfone than the completely crystallized phases as well as the conventional nano-sized TS-1 catalyst suggests their enhanced oxidative activities. The remarkably improved catalytic activity of the intermediately crystallized catalysts can be ascribed to the abundant inter- and intracrystalline mesopores, the surface enriched active hexa-coordinated titanium sites, as well as the absence of anatase species. These could reduce the transport limitation of bulky molecules, and avoid the inefficient decomposition of oxidants.

As shown in Figure S15, the catalyst regenerated with centrifugation shows a decreased activity compared to the fresh one (67% vs. 100%) in the catalytic oxidative desulfurization of DBT, ascribing to the adsorption of reaction product molecules, which may cover some of the surface active sites of the catalyst. However, the catalytic activity can be almost regenerated by calcination in air. After seven reaction-regeneration cycles, the TS-1(H3) catalyst retains ~92% of its initial activity (Figure S16). The XRD, N₂ adsorption desorption and TEM of the TS-1(H3) after the durability test indicate that the catalyst remains the high crystallinity, with slightly decreased mesopore volume (from 0.23 to 0.17 cm^3g^{-1}) and crystallinity (from 100% to 93.2%) (Figures S17-S18 and Tables S1 and S5). UV-vis spectrum shows that the titanium in the used catalyst remains as tetra-coordinated (220 nm) and hexa-coordinated states (270 nm), without the formation of anatase species. ICP measurement indicates that there is slight leaching of the titanium, with ~92% of the initial Ti remained in the TS-1(H3) sample recycled for seven times (Table S1). However, the activity decreases to ~85% when the catalyst is recycled for ten times, which may be ascribed to the obviously reduced crystallinity and titanium content (Figure S19 and Tables S1 and S5).

With the understanding that the intermediately crystallized zeolite catalysts can enhance the oxidative desulfurization

reactions, we further apply this intermediately crystallization method in improving the catalytic activity of conventional nano-sized TS-1 and Ti-Beta zeolite catalysts (Figures S20-S22). Strikingly, both the intermediately crystallized catalysts are enriched with hexa-coordinated titanium, exhibit higher external surface area than the completely crystallized ones and free of anatase phase. As expected, the intermediately crystallized titanosilicates show enhanced catalytic activity towards the desulfurization of DBT with the TON of 7.1 and 16.1 at 30 min respectively, compared with the completely crystallized catalysts (3.1 and 13.9) (Figure S23 and Table S6). Above studies demonstrate that the intermediate crystallization is beneficial for the formation and stabilization of active hexa-coordinated titanium and hierarchical structures with higher external surface area, as well as inhibiting the formation of anatase phase. These features are favorable for oxidative desulfurization enhancing the of bulky organosulphides.

Conclusions

In summary, we present a facile intermediate crystallization strategy for the synthesis of nano-sized hierarchical TS-1 zeolites free of anatase species with the seed-assisted method. The catalytic properties of oxidation of DBT and 4,6-DMDBT are greatly dependent on the catalysts prepared at different crystallization time. The intermediately crystallized catalyst with abundant inter- and intracrystalline mesopores, the surface enriched active titanium species, as well as the absence of anatase species, give rise to significantly higher catalytic activity than the completely crystallized analogue. This suggests that the completely crystallized zeolite catalysts are not always expected to have the best catalytic performance. This work provides a useful guidance to explore highly efficient catalysts by modulating the crystalline states.

Conflicts of interest

There are no conflicts to declare.

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