Supporting Information

Impact of Polymer Modifier on Directing Non-classical Crystallization Pathway of TS-1 Zeolite: Accelerating Nucleation and Enriching Active Sites

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Experimental section

Reactant agents. Tetraethyl orthosilicate (TEOS, Sinopharm), tetrabutyl orthotitanate (TBOT, Sinopharm, 98%), tetrapropylammonium hydroxide solution (TPAOH; Guangfu Fine Chemical Research Institute, 25 wt%), cationic polyacrylamide (PAM; MW=8000000-15000000, Guangfu Fine Chemical Research Institute), cationic polyacrylamide (PAM, MW=8000000, Adamas), cationic polyacrylamide (PAM, MW=18000000, Adamas), acrylamide (AM, Tianjin Fuchen Chemical Reagent Factory), polydimethyldiallyl ammonium chloride (PDDA, MW=400000-500000, Aladdin, 20 wt%), polyethyleneimine (PEI, MW=10000, Aladdin, 99 %), anatase (Alfa Aesar, 99.9 %), HCl (Beijing Chemical Works, 36 wt%), dibenzothiophene (DBT, Innochem Science & Technology), Tert-butyl hydroperoxide (TBHP, 70 wt% aqueous solution, Alfa Aesar (China) Chemicals), n-octane (Tianjin Fuchen Chemical Reagent Factory), n-hexadecane (Tianjin Fuchen Chemical Reagent Factory), 1-hexene (Aladdin, 99 %), methanol (Tiantai Fine Chemical Research Institute, 99.5 %) and n-dodecane (Aladdin). All the above materials were purchased commercially and used directly without further purification.

Syntheses of PAM-assisted TS-1 zeolites. PAM-assisted TS-1 zeolite was synthesized through a two-step hydrothermal route under static conditions from the starting gels with the molar compositions of SiO$_2$: 0.033 TiO$_2$: 0.27 TPAOH: 30 H$_2$O: 0.1 PAM. Typically, the TPAOH solution was mixed with water under stirring. Then, TBOT and TEOS were added to the TPAOH solution to form a clear solution under continuous stirring. After complete hydrolysis of TEOS and TBOT, PAM was added into the above solution. The reaction mixture was further stirred for another 24 hours until the solution becomes uniform. Finally, the resulting solution was transferred into a Teflon-lined stainless-steel autoclave and then crystallized in a pre-heated oven at 80 °C for 3 hours, and then at 120 °C for 3 hours under static conditions. The as-synthesized solid products were centrifuged, washed with distilled water several times, and dried at 80 °C in an oven overnight, then followed by calcination at 550 °C for 6 hours. This sample is named as P-10-80-120. Furthermore, samples with different PAM additions were also synthesized by using the similar synthetic method, which are defined as P-x-80-120, where x represents the molar ratio of PAM to SiO$_2$ times $10^2$ employed in the synthesis.
In order to reveal the effect of the molecular weight of PAM polymer and other polymers on the crystallization of TS-1, TS-1 zeolites with different polymers were synthesized under the same conditions as P-10-80-120. The detailed synthetic conditions for these samples are listed in Table S1.

In order to reveal the role of PAM in the synthesis of TS-1 zeolite, TS-1 zeolites in a two-step crystallization with different times, and a single crystallization at 120 °C and at 170 °C have been prepared. Also, pure silicon silicalite-1 zeolite (named as P-S-10-80-120), and traditional microporous TS-1 (named micro-TS-1) have been synthesized for comparison. The detailed synthetic conditions for these samples are listed in Table S1.

**Syntheses of control and acid treated TS-1 zeolites.** Control TS-1 zeolite named P-0-80-120 was synthesized with the same molar composition of the P-10-80-120 sample without adding PAM. The control sample was crystallized in a pre-heated oven at 80 °C for 3 hours, and then at 120 °C for 6 hours under static conditions. In addition, to explore the influence of TiO$_6$ species on catalytic activity of TS-1 zeolite, the sample of P-10-80-120 was washed to eliminate most TiO$_6$ species. Typically, 1 g P-10-80-120 sample was treated with 100 mL 1M HCl water solution at room temperature for 6 h, and then thoroughly washed with distilled water.

**Characterizations**

The crystallinity and phase purity of the samples were determined by powder X-ray diffraction (XRD) on Rigaku Ultima IV diffractometer with Cu Ka radiation ($\lambda=1.5418$ Å). Nitrogen adsorption/desorption measurements were carried out on a Micromeritics 2020 analyzer at 77.3 K after degassing the samples at 350 °C under vacuum. Chemical compositions were determined by Inductively Coupled Plasma (ICP) analysis using an iCAP 7000 SERIES. X-ray photoelectron spectroscopy (XPS) was performed with an ESCALAB 250 X-ray photoelectron spectrometer using Al as the excitation source. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were collected using a JSM-6510 (JEOL) electron microscope and a FEI Tecnai F20 electron microscope operating at an acceleration voltage of 200 kV, respectively. Atomic Force Microscope (AFM) images were recorded in the tapping mode from Dimension Fastscan Bio (Bruker) under ambient conditions. X-ray absorption near-edge structure (XANES) spectra at the Ti K-edge were performed using the Sector 20-BM beamline of the
Advanced Photon Source at Argonne National Laboratory (Argonne, IL). The beamline was equipped with a doublecrystal Si(111) monochromator. A 12-element Ge fluorescence detector was used to collect the spectra of the Ti K-edge. The energy was calibrated according to the absorption edge of a pure Ti foil as a reference. Data processing and EXAFS fitting were performed using the Athena, Artemis and Igor software. Elemental analysis of samples was investigated by the X-ray energy dispersive spectra (EDS, Quantax EDS spectroscopy, Bruker). Ti species were investigated by UV-vis diffuse reflectance spectroscopy (UV-Vis) over a range of 200 to 600 nm using a SHIMADZU U-4100. The baseline correction was carried out with powder BaSO₄. Fourier transform infrared (FT-IR) spectra were recorded on a BRUKER vertex 80v, samples were pelleted with KBr powder before testing. Thermal gravimetric (TG) analyses were performed using a TA TGA Q500 at temperatures ranging from room temperature to 800 °C at a heating rate of 10 °C min⁻¹. ²⁹Si solid state magic angle rotation nuclear magnetic resonance (SS MAS NMR) and ¹H→¹³C CP MAS NMR were collected on Bruker Avance NEO 600WB system. Kaolin and Adamantane (Adam) was used as the standard sample of ²⁹Si and ¹³C, respectively. And the calibration of ²⁹Si and ¹³C were -91.4 ppm and 38.48 ppm, respectively. For the liquid NMR measurement of the supernatant of sample, the supernatant was mixed with deuterium oxide (D₂O) for field locking, and then placed in polytetrafluoroethylene (PTFE) sample tubes for NMR measurement. Tetramethylsilane was used as standard sample, the calibration of ²⁹Si was 0 ppm The dynamic light scattering test was carried out on Malvern Zetaszier Nano-ZS.

Catalytic tests

Oxidative desulfurization of dibenzothiophene (DBT). A certain amount of DBT was dissolved in n-octane to prepare the model fuel with the concentration of sulfur is about 500 ppm. The ODS reactivity was tested in a 25 mL two-neck glass flask equipped with a reflux condenser. In a typical run, the reaction was carried out with 10 mL model fuel, 0.10 g of zeolite catalyst, 0.028 g of n-octadecane and 0.028 g of TBHP at 353 K for 120 min. Afterwards, GC-MS (Thermo Fisher Trace ISQ, equipped with a TG-5MS column, 60 m 320 μm 25 μm) was utilized to analyse the reactant and products.

Epoxidation of 1-hexene. Epoxidation of 1-hexene with H₂O₂ as oxidant was carried out in a 25 mL round-bottom flask equipped with a reflux condenser. In a typical operation, 0.05 g of catalyst, 10 mL of
methanol, 10 mmol of 1-hexene and 3.3 mmol H₂O₂ (30 wt%) were added into a double-necked round bottom flask in sequence, and the reaction was carried out under continual magnetic stirring at 333 K for 120 min. Upon completion of the reaction, the liquid product was centrifuged and analyzed by GC-MS (Thermo Fisher Trace ISQ, equipped with a TG-5MS column, 60 m 320 μm 25 μm) and n-dodecane as internal standard. The conversion of 1-hexene and the selectivity of corresponding epoxy compounds were calculated. The conversion and efficiency of H₂O₂ were determined by iodometric method.
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Note: The induction period of nucleation was estimated from the powder XRD pattern of the extracted solid according to the initial characteristic diffraction peak. Since no crystal appeared in P-0-80-120 before 6 h (120 °C), the induction time was determined to be 9 h (80 °C for 3 h and 120 °C for 6 h), while P-10-80-120 was 4.5 h (80 °C for 3 h and 120 °C for 1.5 h).
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Table S1. Molar compositions of the initial reaction mixtures and crystallization conditions of TS-1 zeolites.\textsuperscript{a}

|                | SiO\textsubscript{2} | TiO\textsubscript{2} | Name of CGM | CGM | Temperature (time)          |
|----------------|----------------------|----------------------|-------------|-----|-----------------------------|
| P-0-80-120     | 1                    | 0.033                |             |     | 80 °C (3 h) + 120 °C (6 h)  |
| P-5-80-120     | 1                    | 0.033                | PAM\textsuperscript{b} | 0.05 | 80 °C (3 h) + 120 °C (3 h)  |
| P-10-80-120    | 1                    | 0.033                | PAM         | 0.10 | 80 °C (3 h) + 120 °C (3 h)  |
| P-20-80-120    | 1                    | 0.033                | PAM         | 0.20 | 80 °C (3 h) + 120 °C (3 h)  |
| P-0-120        | 1                    | 0.033                |             |     | 120 °C (6 h)                |
| P-10-120       | 1                    | 0.033                | PAM         | 0.10 | 120 °C (3 h)                |
| P-0-170        | 1                    | 0.033                |             |     | 170 °C (3 h)                |
| P-10-170       | 1                    | 0.033                | PAM         | 0.10 | 170 °C (3 h)                |
| AM-10-80-120   | 1                    | 0.033                | AM          | 0.10 | 80 °C (3 h) + 120 °C (12 h) |
| P800-10-80-120 | 1                    | 0.033                | PAM         | 0.10 | 80 °C (3 h) + 120 °C (3 h)  |
|                |                      |                      | (MW=8000000) |     |                             |
| P1800-10-80-120| 1                    | 0.033                | PAM         | 0.10 | 80 °C (3 h) + 120 °C (8 h)  |
|                |                      |                      | (MW=18000000) |    |                             |
| PEI-10-80-120  | 1                    | 0.033                | PEI         | 0.10 | 80 °C (3 h) + 120 °C (6 h)  |
| PDDA-10-80-120 | 1                    | 0.033                | PDDA        | 0.10 | 80 °C (3 h) + 120 °C (8 h)  |
| P-S-10-80-120  | 1                    | 0                    | PAM         | 0.10 | 80 °C (3h) + 120 °C (3h)    |
| micro-TS-1     | 1                    | 0.014                |             |     | 170 °C (36 h)               |

\textsuperscript{a}The ratios of TPAOH/SiO\textsubscript{2} and H\textsubscript{2}O/SiO\textsubscript{2} are 0.27 and 30, respectively. The ratio of H\textsubscript{2}O/SiO\textsubscript{2} is 124 for micro-TS-1.

\textsuperscript{b}Unless particularly stated, the MW of PAM is 8000000-15000000.
Table S2. Textural properties of synthesized TS-1 samples.

|        | Si/Ti<sup>a</sup> | \(S_{\text{BET}}\) \(\text{(m}^2\text{ g}^{-1})\)<sup>b</sup> | \(S_{\text{micro}}\) \(\text{(m}^2\text{ g}^{-1})\)<sup>c</sup> | \(S_{\text{ext}}\) \(\text{(m}^2\text{ g}^{-1})\)<sup>c</sup> | \(V_{\text{total}}\) \(\text{(cm}^3\text{ g}^{-1})\)<sup>d</sup> | \(V_{\text{micro}}\) \(\text{(cm}^3\text{ g}^{-1})\)<sup>e</sup> | \(V_{\text{meso}}\) \(\text{(cm}^3\text{ g}^{-1})\)<sup>f</sup> |
|--------|-------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|----------------------------------|
| P-0-80-120 | 107               | 389                              | 276                              | 112                              | 0.49                             | 0.15                             | 0.34                             |
| P-5-80-120 | 52                | 369                              | 228                              | 141                              | 0.50                             | 0.10                             | 0.40                             |
| P-10-80-120| 29                | 339                              | 232                              | 106                              | 0.40                             | 0.09                             | 0.31                             |
| P-20-80-120| 26                | 276                              | 189                              | 88                               | 0.16                             | 0.07                             | 0.09                             |

<sup>a</sup>The elemental compositions in the bulk were determined by ICP, <sup>b</sup>Surface area was calculated from the nitrogen adsorption isotherm using the BET method; <sup>c</sup>\(S_{\text{micro}}\) (micropore area), \(S_{\text{ext}}\) (external surface area) were calculated using the t-plot method. <sup>d</sup>\(V_{\text{total}}\) (total pore volume) at \(P/P_0 = 0.99\); <sup>e</sup>\(V_{\text{micro}}\) (micropore volume) was calculated using the t-plot method. <sup>f</sup>\(V_{\text{meso}}\) (mesopore volume) = \(V_{\text{total}}\) (total pore volume) - \(V_{\text{micro}}\).
Table S3. Si/Ti ratio of synthesized samples.\textsuperscript{a}

| Sample            | Crystallization time (80 °C) | Crystallization time (120 °C) | Si/Ti |
|-------------------|-----------------------------|-----------------------------|-------|
| AM-10-80-120      | 3 h                         | 12 h                        | 85    |
| P800-10-80-120    | 3 h                         | 3 h                         | 28    |
| P1800-10-80-120   | 3 h                         | 6 h                         | 59    |
| PEI-10-80-120     | 3 h                         | 6 h                         | 69    |
| PDDA-10-80-120    | 3 h                         | 8 h                         | 126   |

\textsuperscript{a}The elemental compositions in the bulk were determined by ICP.
Table S4. Oxidation of 1-hexene over synthesized TS-1 samples.\(^a\)

|                  | Conv. (%) | Sel. (%) | \(\text{H}_2\text{O}_2\)       |
|------------------|-----------|----------|-------------------------------|
|                  | Max (%)   | Conv. (%)| Effic. (%)                    |
| P-0-80-120       | 18.3      | >99      | 22.7                          | 80.6 |
| P-5-80-120       | 20.0      | 99       | 27.6                          | 72.5 |
| P-10-80-120      | 26.5      | 98       | 36.2                          | 73.2 |
| P-10-80-120-HCl  | 21.4      | 99       | 25.7                          | 83.3 |
| P-20-80-120      | 2.30      | >99      | 15.2                          | 15.1 |
| \(\text{TiO}_2\) | 1.01      | >99      | 18.2                          | 5.5  |

\(^a\)Reaction conditions: cat., 50 mg; 1-hexene, 10 mmol; \(\text{H}_2\text{O}_2\) (35 wt%), 3.3 mmol; methanol, 8.0 g; temp., 333 K.