Crystallization of as-Mesocellular Silica Foam into Hierarchical TS-1 Zeolites by Conventional Hydrothermal and Dense-Gel Routes for Oxidation Reactions

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ABSTRACT: Crystallization of as-mesocellular silica foam (as-MCF) into TS-1 zeolites by conventional hydrothermal and dense-gel routes is reported. The TS-1 synthesized through the dense-gel route (TS-1-d) showed higher meso-macroporosity (0.311 vs 0.233 cm$^3$/g), smaller particle size (130 vs 305 nm), and enhanced external surface area (86 vs 31 m$^2$/g) than that synthesized under conventional hydrothermal conditions (TS-1-h). These might suggest that an organic template from as-MCF acted as mesoporogen in the dense-gel synthesis; however, segregation of the organic template and the synthesis mixture occurred in the conventional hydrothermal synthesis. The obtained TS-1 from the crystallization of as-MCF showed an enhanced framework Ti. The turnover frequencies (h$^{-1}$) of TS-1-d toward hydroxylation of phenol and oxidation of dibenzothiophene (DBT) were 2 and 5 times, respectively, higher than those by TS-1-h. The DBT conversion by TS-1-d reached >99.0%, while it was only 63% by TS-1-h, suggesting the potential of TS-1-d for deep desulfurization of the fuels. Consequently, the crystallization of as-mesoporous materials through the dense-gel route is a promising approach to prepare TS-1 zeolites with smaller particle sizes and enhanced mesoporosity.

1. INTRODUCTION

Zeolites are microporous crystalline metallosilicates with shape selectivity, hydrothermal stability, and adjustable acidity characters, which are used in catalysis, adsorption, and ion-exchange processes. These materials are mainly synthesized through conventional hydrothermal processes by mixing silicon and heteroatom precursors in a bulk basic aqueous medium followed by aging at the temperatures (>100 °C) in a sealed autoclave to transform amorphous materials into crystalline zeolites. In the hydrothermal process, water plays the role of the mineralizing agent and the carrier of heat and mass transfer. Titanosilicate-1 (TS-1) zeolite, obtained by Ti substitution of Si in silicalite-1, with MFI topology and Lewis acidic characters has been prepared through a conventional hydrothermal process. The TS-1 is active and selective in the hydroxylation of aromatic compounds, epoxidation of alkenes, ammoximation of ketones, oxidative desulfurization of fuels, and so forth. The Catalytic performance of TS-1 is strongly influenced by the amount and accessibility of the substrates to framework Ti active sites. An increase in substrate accessibility to the active sites is achieved by making intracrystalline mesoporosity with the use of hard and soft templates and nanozeolites aggregates by adjusting the chemical composition of the synthesis gel and control over operational conditions through the hydrothermal processes. The conventional hydrothermal synthesis of TS-1 zeolite, however, suffers from challenges of simultaneous control over enhanced framework Ti and small crystal sizes, using autogenous pressure reactors, generation of large amounts of wastewater, and low yield of solid materials.

The alternative strategies for the hydrothermal synthesis of zeolites are dense-gel and solvent-free routes, which are conducted in the absence of bulk water and thus have the advantages of less wastewater generation, higher yields of solid materials, the possibility of working at higher temperatures, and faster synthesis. The synthesis of several zeolites including TS-1 by these approaches have been reported by many research groups. For example, the solvent-free synthesis of TS-1 zeolite by seeding resulted in crystals of sizes in the range of 300−500 nm and the synthesis of zeolite beta through the dense-gel route, containing a tiny amount of water, resulted in aggregates of nanoparticles in the range of 50−500 nm. However, the presence of any water either in solvent-free or dense-gel is controversial, and thus, the role of water has been investigated by several research groups.

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the formation of water by, for example, the condensation of silanol groups of silica precursors during the solvent-free synthesis, suggesting that zeolites cannot be synthesized if a trace of water is absent.\textsuperscript{8a,11} Nevertheless, the solvent-free synthesis of TS-1 zeolite faces challenges of low amount of framework Ti and less control over the crystal sizes.

The properties of silica precursors and the presence of additives such as polymers in the synthesis gel control physicochemical properties of the zeolites by influencing the nucleation and crystal growth\textsuperscript{12} and creating mesoporosity.\textsuperscript{13} The crystallization of silica-based mesoporous materials, with high surface area and acidic property, through the hydrothermal process resulted in zeolites with enhanced catalytic performances.\textsuperscript{14} The aim of this study was to understand the possible synergistic impacts of the organic template and silica wall of as-mesoporous materials on the physicochemical properties of TS-1 zeolites through conventional hydrothermal and dense-gel routes. The crystallization of as-mesocellular foam silica (as-MCF), MCF containing organic templates, into TS-1 zeolite through conventional hydrothermal and dense-gel routes was conducted for the first time. MCF has a three-dimensional, interconnected cavity structure with cage-like pores (20–50 nm), which are connected by windows of 8–20 nm.\textsuperscript{15} As-MCF was synthesized using an organic template of \( \text{H} \left( \text{CH}_2\text{CH}_2\text{O} \right)_{10} \left( \text{CH}_2\text{CH} \left( \text{CH}_3 \right) \text{O} \right)_{70} \left( \text{CH}_2\text{CH}_2\text{O} \right)_{20} \text{H} \) (Pluronic P123) based on the procedure reported previously (Supporting Information).\textsuperscript{16} The crystallization of as-MCF through the dense-gel route resulted in TS-1 with a smaller particle size, higher mesoporosity, and higher yield of solid material than that obtained under the hydrothermal process. The TS-1 synthesized through the dense-gel route (TS-1-d) showed superior catalytic performances in the hydroxylation of phenol into catechol and hydroquinone and the oxidation of dibenzothiophene (DBT) into dibenzothiophene sulfoxide over that synthesized under conventional hydrothermal processes (TS-1-h).

2. RESULTS AND DISCUSSION

The TS-1 samples synthesized through conventional hydrothermal and dense-gel routes were characterized by several techniques. The X-ray diffraction (XRD) patterns of TS-1-h and TS-1-d synthesized through conventional hydrothermal and dense-gel routes, respectively, are shown in Figure 1. The XRD patterns were recorded at 2\( \theta \) angles between 4 and 70\( ^\circ \) presenting five characteristic diffraction peaks of MFI topology\textsuperscript{17} at 2\( \theta \) of 7.742, 8.64, 22.94, 23.68, and 24.21\(^\circ\). The XRD results thus suggested successful synthesis of TS-1 zeolites. The diffraction peaks of TS-1-h showed higher intensity than that of TS-1-d, possibly suggesting a bigger crystal size for TS-1-h. The XRD pattern also showed no detectable diffraction peak at 2\( \theta \) of 25.4\(^\circ\), within the sensitivity of the instrument, suggesting the absence of the anatase TiO\(_2\) phase.

Field emission scanning electron microscopy (FE-SEM) and scanning electron microscopy (SEM) studies of the obtained TS-1 samples were conducted to investigate the morphology and size of the particles. The SEM investigation of the TS-1 samples showed aggregates (10–50 \( \mu \)m) of nanosized particles for both TS-1-h and TS-1-d (Figure S1). The SEM (Figure S1) and FE-SEM investigation of TS-1 samples showed no presence of MCF particles (Figure 2), suggesting full crystallization of MCF into TS-1 zeolite. The FE-SEM study of TS-1-h showed a wider range of particle sizes and irregular morphology of merged oval, spherical, cuboid, and rounded rectangular; however, TS-1-d showed more uniform particle sizes and relatively regular spherical- and oval-like morphology. The average particle size of TS-1-h and TS-1-d obtained by FE-SEM were 305 and 130 nm, respectively. This is because the particle size and morphology change upon dilution and pH of the synthesis gel.\textsuperscript{18} The much smaller particle size of TS-1-d than that of TS-1-h is possibly coming from the higher nucleation rate by the higher pH (11.6 vs 10.5) of the synthesis gel.\textsuperscript{19} The lower pH of the synthesis gel under hydrothermal conditions possibly caused slower dissolution of as-MCF and consequently nonhomogeneous nucleation and growth rates led to irregular shapes and wider and bigger particle sizes. Consequently, the crystallization of as-MCF into TS-1 zeolite through the dense-gel route resulted in smaller crystal sizes and a uniform morphology.

The physical properties of the parent MCF and TS-1 samples were characterized by both \( \text{N}_2 \) adsorption–desorption and SAXS techniques. The \( \text{N}_2 \) adsorption–desorption isotherms with pore size distribution (PSD) of TS-1 and MCF are shown in Figures 3 and S2, respectively. Summary of the physical properties taken from \( \text{N}_2 \) adsorption–desorption isotherms is given in Table S1. The isotherms of TS-1 samples and MCF were type IV based on the IUPAC classification, indicative of micromesoporous materials. The \( \text{N}_2 \) adsorption–desorption of the TS-1 samples in comparison with that of MCF showed significant decrease in the total \( \text{N}_2 \) adsorption (Table S1; 1.26 vs 0.468 cm\(^3\)/g), however, much higher \( \text{N}_2 \) adsorption at the relative pressure of \( P/P_0 < 0.02 \) is a characteristic of micropore zeolites. The \( \text{N}_2 \) adsorption–desorption isotherms thus in line with XRD and FE-SEM results suggested the crystallization of as-MCF into TS-1 zeolites. The TS-1-d showed higher total pore volume (Table S1; 0.468 vs 0.409 cm\(^3\)/g) and larger total surface area (487 vs 449 m\(^2\)/g) than that by TS-1-h. The bigger hysteresis loop with closure at the lower relative pressure of TS-1-d presented higher meso/macroporosity than that of TS-1-h (Table S1; 0.311 vs 0.233 cm\(^3\)/g). The PSD of TS-1 materials showed similar trend with that of MCF (Figures 3 and S2); however, in case of TS-1-h, the majority of the voids was shifted to the range of macropore sizes. The external surface area of TS-1-d was much higher than that of TS-1-h (86 vs 31 m\(^2\)/g) coming from its smaller

Figure 1. XRD patterns of TS-1-h and TS-1-d.
particle sizes. The possible formation of mesoporosity in TS-1 materials and parent MCF was furthermore investigated by the use of SAXS (Figure S3). The SAXS results of TS-1-d showed a scattering peak at 2θ of about 0.74° similar to that of MCF but with smaller intensity, indicating the presence of ordered mesoporosity. These results might suggest that the organic template of Pluronic P123 from the parent as-MCF was possibly retained inside the synthesis mixture and acted as mesoporogen in the dense-gel synthesis (Figure S4). The SAXS investigation of TS-1-h showed no detectable scattering peak, indicating the absence of mesoporosity, which might come from the segregation of the organic template and the synthesis mixture during the conventional hydrothermal synthesis (Figure S4). Consequently, the results suggested that the dense-gel crystallization of as-mesoporous materials is a strong approach to synthesize mesoporous nanosized TS-1 zeolite.

The presence of framework Ti, a type of Ti species, and the amount of total Ti of TS-1 samples were analyzed by Fourier transform infrared (FTIR), diffuse reflectance UV−vis (DR UV−vis), and inductively coupled plasma atomic emission spectroscopy (ICP-AES) techniques, respectively. The FTIR spectra of TS-1 typically shows absorption peaks at 550, 800, and 960 cm$^{-1}$. The absorption peaks at 960 and 800 cm$^{-1}$ are attributed to nonsymmetric vibration of Si−O−Ti and symmetric stretching of Si−O−Si, respectively. However, the silicalite-1 shows no absorption peak at 960 cm$^{-1}$. The absorption peak at 550 cm$^{-1}$ is characteristic of MFI topology. The relative intensity of the absorption peak at 960 cm$^{-1}$ to that at 800 cm$^{-1}$ ($I_{960}/I_{800}$) is a known parameter of relative proportion of framework Ti. The FTIR spectra of TS-1-h and TS-1-d (Figure S5) showed absorption peaks at 550, 800, and 960 cm$^{-1}$, suggesting successful incorporation of Ti in the tetrahedral coordination (framework Ti). The intensity of the $I_{960}/I_{800}$ ratio of TS-1-h and TS-1-d were 1.59 and 1.42, respectively, suggesting higher framework Ti for the TS-1-h. The ICP-AES technique in line with FTIR indicated higher total Ti for TS-1-h than that for TS-1-d [2.08 vs 1.85 mol.%, Ti/(Si + Ti)]. The higher framework Ti content of TS-1-h than that of TS-1-d possibly in part is coming from the lower pH of the synthesis mixture, which decrease the Ti precursors hydrolysis rate and thus harmonize the hydrolysis of precursors and crystallization processes to increase Ti
incorporation. The dense gel of the synthesis mixture might also contributed in the lower incorporation of framework Ti of TS-1-d by decrease in the transfer rate of Ti species in comparison with that of TS-1-h. The DR UV–vis spectra of the TS-1 samples (Figure S6) showed absorbance at about λ = 220 nm for both TS-1-h and TS-1-d corresponding framework Ti and almost no absorbance at about λ = 310 nm, indicating the absence of the anatase TiO2 phase. The obtained TS-1 materials by the transformation of as-MCF showed higher framework Ti than that by either TEOS and/or MCF (Table S2), suggesting the synergetic impact of the organic template and silica wall of MCF in the enhancement of framework Ti. The efficient synthesis of a catalyst provides the enhancement of both the yield of solid materials and catalytic performance. The yield of solid materials of TS-1-d and TS-1-h were 1.1 and 0.98 g-TS-1/g-TPAOH, respectively. This is in accordance with the increased yield of solid materials by the solvent-free synthesis by the other research groups. The lower yield of solid materials of TS-1-h in comparison with that of TS-1-d might come from significant amounts of dissolved silica and titanium species in the aqueous medium above the solid materials in the conventional hydrothermal synthesis. An increase in framework Ti and accessibility to the active sites of TS-1 zeolite are desirable to enhance the catalytic performance. The catalytic activity of TS-1 were then evaluated toward the hydroxylation of phenol (kinetic diameter of 0.57 nm) and oxidation of DBT (kinetic diameter of 0.9 nm). The TS-1-d showed much superior catalytic performances over TS-1-h (Figure 4 and Table S3). Turnover frequency (TOF) (h⁻¹) of phenol hydroxylation by TS-1-d and TS-1-h were 8.34 and 4.76 h⁻¹, respectively. The conversion of phenol reached to 25.0 and 20.0% for TS-1-d and TS-1-h, respectively (Figure 4). The higher catalytic activity of TS-1-d than that of TS-1-h toward the hydroxylation of phenol is coming from the beneficial effects of higher external surface area by a few times and enhanced mesoporosity, while the adverse effect of the lower framework Ti content of TS-1-d was only 11%. The TOF (h⁻¹) of TS-1-d and TS-1-h in DBT oxidation were 4.3 and 0.85, respectively. The kinetic diameter of DBT (0.9 nm) is bigger than the micropore of TS-1 (0.56 nm); thus, most of the DBT oxidation occurs on the external surface and pore mouth and much higher surface area of TS-1-d accounts for its much higher activity. The conversion of DBT by TS-1-d was 99.0%, while it was only 63.0% by TS-1-h. Consequently, the TS-1-d synthesized through the dense-gel route showed higher yield of solid materials and a superior catalytic performance.

3. CONCLUSIONS

The crystallization of as-MCF into TS-1 zeolites was investigated through conventional hydrothermal and dense-gel routes. The TS-1-d in comparison with TS-1-h showed a smaller particle size, higher mesoporosity, and higher yield of solid material. Both TS-1-d and TS-1-h synthesized by the use of as-MCF presented enhanced framework Ti. The TS-1-d showed much superior catalytic performances in the oxidation of phenol and DBT than those by TS-1-h. Consequently, the crystallization of as-mesoporous materials through the dense-gel route is a strong alternative to synthesize TS-1 with small particle sizes and enhanced mesoporosity for efficient catalytic performances.

ASSOCIATED CONTENT

Supporting Information

Details of synthesis of TS-1 and MCF materials, characterization, and catalytic tests (PDF)

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Notes

The authors declare no competing financial interest.

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