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Engineering Mesopore Formation in Hierarchical Zeolites under High Hydrostatic Pressure

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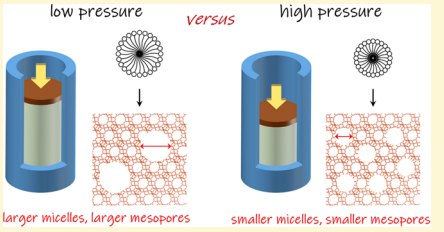
ABSTRACT: Tailoring the textural properties of porous materials is of paramount importance to optimize their performance in a variety of applications. To this end, critical synthesis parameters influencing crystallization and reorganization of porous materials need to be identified and judiciously controlled. Although the effect of pressure on chemical transformations is ubiquitously present, its impact on fabricating porous materials with tailored physicochemical properties remains unexplored and its potential untapped. In this work, we disclose a detailed study on the effects of high hydrostatic pressure on the formation of well-controlled intracrystalline mesopores in ultrastable Y (USY) zeolite by the so-called surfactant-templating method. The rate of mesopore formation significantly increases upon elevating the pressure, whereas the average size of the mesopores—directed by the self-assembly of the surfactant—decreases. By simultaneously adjusting the external pressure and selecting surfactants of different lengths, we have been able to precisely control the mesopore size in the USY zeolite. Our findings clearly show that external hydrostatic pressure can be used to both accelerate mesopore formation and engineer their size with subnanometer precision. As a second example, we investigated the effect of external pressure on the synthesis of MCM-41. The results on MCM-41, consistent with our observations on the USY zeolite, further confirm that the use of high external pressure greatly affects the self-assembly behaviors of the amphiphilic molecules involved in the synthesis/modification of the porous materials. Our results show that the high-pressure approach represents an untapped opportunity for synthesis/modification of functional porous materials that will likely yield new discoveries in this field.



INTRODUCTION

Pressure is a critical parameter to chemical reactions, as it governs both thermodynamic and kinetics aspects.[1] According to the van't Hoff equation, elevating pressure favors the equilibrium to move forward for a reaction with a negative reaction volume.[2] For a long time, this principle has often been practiced in gas-phase reactions, such as ammonia synthesis and production of polyethylene. Upon high pressure, geometrical confinements can be generated to molecules in the liquid and solid phases, which alter the electronic structures of molecules, modulate intermolecular interactions, and change the overall free energy landscape.[3] These high-pressure effects lead to reaction outcomes that could not be possible at ambient pressure, such as artificial syntheses of diamond and boron nitride.[4] Most of the high-pressure syntheses involve dense crystals where atoms are arranged in close-packed symmetries. Few studies have been targeted at open framework materials, which are a class of materials featuring ordered inorganic or hybrid structures that form nanosized pores, channels, and cages. Representative open framework materials include zeolites, mesoporous oxides, and metal−organic frameworks (MOFs).[5] Tailoring physicochemical properties of open framework materials is of paramount importance to optimize their performance in diverse applications. In particular, precise pore engineering is of great significance, as many functions of the open framework materials rely on mechanisms of size recognition or confinement effect, which requires size regulation with high accuracy and over a broad spectrum.[6,7] A number of factors, such as selection of organic templates or ligands, synthesis conditions, and postsynthesis activation/modification procedures, are widely used to influence the pore characteristics of the open framework materials.[8] However, pressure is not considered among these parameters, which renders its impact underestimated and its potential untapped.

Zeolites are a class of open frameworks built upon tetrahedral silicon and aluminum oxides.[9,10] Owing to their high stability, unique pore architecture, and adjustable acidity, zeolites have been widely used in a variety of chemical

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processes.[11−13] To further improve the performance of zeolites in those applications, both hydrothermal synthesis ("bottom-up" approach) and postsynthesis modification ("top-down" approach) have been studied in great detail. The crystallization of zeolites is very sensitive to conditions where hydrothermal synthesis is carried out.[14−16] Recently, we reported the effects of high external pressure on the hydrothermal synthesis of zeolites from alkali-metal-containing aluminosilicate precursors without the addition of any organic molecules, where unique crystallization behaviors contradicting the observations under autogenous pressures were revealed.[17] Organic molecules have played an important role in the synthesis and postsynthesis modification of zeolites. For example, organic molecules have been extensively employed as structure-directing agents for synthesizing zeolites,[18−20] as crystal growth modifiers for tuning the bulky morphology of zeolites,[21,22] and as mesoporogens for creating hierarchical zeolites.[23] Applying high external pressure during both the synthesis and postsynthesis modification of zeolites in the presence of organic compounds is expected to offer untapped opportunities.

Herein, we report the use of surfactants under high external pressure to introduce tunable mesoporosity in ultrastable Y (USY) zeolite and porous silica and provide new insights into organic−inorganic interactions that determine the pore size and architecture of the templated materials. We first present a systematic study on the effect of high hydrostatic pressure on the surfactant templating of the USY zeolite. The surfactant-templating process is a well-known postsynthetic strategy that allows for introducing large amounts of tunable mesoporosity in zeolites while preserving their most important properties. The mesopores generated by this method have an average pore size corresponding to the micelle size.[24−26] This feature allows us to reveal how the assembly of the surfactant molecules to form micelles evolves in response to high external pressures and consequently alters the mesopore size of the zeolite. To gain additional insights into the impact of high pressure on the packing behavior of the surfactants and the size of the mesopores produced by micelles, we carried out a second study, in which we focused on the synthesis of ordered mesoporous silica MCM-41, which further confirmed our conclusions. Because the size of its mesopores is determined by the size of the micelles used to prepare it,[27] the study on MCM-41 provides a fundamental and simple method to study the role of external pressure on the micelle size and therefore on the mesopore size of the surfactant-templated USY zeolite.

EXPERIMENTAL SECTION

Materials. CBV720 (USY) was provided by Zeolyst with a Si/Al ratio of 15. Sodium hydroxide (NaOH), octyltrimethylammonium bromide, dodecyltrimethylammonium bromide, tetradecyltrimethylammonium bromide, cetyltrimethylammonium bromide (CTAB), and octadecyltrimethylammonium bromide were purchased from Wako Pure Chemical Industries (Ltd.). All chemicals were used without further purification. Deionized water was used in all experiments.

Apparatus. A homemade warm isostatic press (WIP, see Figure S1) was used as the pressurization apparatus, and deionized water was used as the pressure medium. The maximum treatment temperature was 150 °C, and the pressure was 200 MPa. A Teflon tube was purchased from MISUMI and used as the reaction vessel (see Figure S2). The Teflon tube was heat-sealed at 330 °C at both ends, which were further sealed with metal clips. The sealed Teflon tube was then placed in the chamber of the WIP.

Surfactant Templating of the USY Zeolite. In a typical run, 0.09 g of CTAB was dissolved in 3.42 g of NaOH solution (0.49 wt %) followed by stirring for 30 min. Thereafter, 0.18 g of parent zeolite (Zeolyst CBV720, Si/Al ratio of 15) was added, giving a mixture with a molar ratio of 1 TO_2:0.082 CTAB:0.14 NaOH:75 H_2O (TO_2 represents SiO_2 and $1/2Al_2O_3$). Subsequently, the mixture was sealed in a Teflon vessel and then placed in a high-pressure treatment apparatus. The treatment was performed at a certain temperature (50−150 °C) for 30 min to 120 h under different pressures from autogenous pressure to 200 MPa. After the treatment, the product was washed with deionized water and recovered by centrifugation and drying. The recovered zeolites were calcined at 550 °C for 5 h in a muffle oven.

Synthesis of MCM-41. In the synthesis under autogenous pressure, CTAB (0.8 g) was dissolved in a NaOH aqueous solution (0.1 M, 42.8 mL), which was vigorously stirred at 40 °C for 20 min. Thereafter, tetraethyl orthosilicate (TEOS, 3.81 g) was added dropwise to the previous solution. The resultant white slurry was first stirred at 40 °C for 2 h and then heated at 100 °C for 24 h. The solid precipitates were recovered by vacuum filtration, washed with deionized water, and dried at 80 °C before calcination at 550 °C for 5 h to remove the organic template. In the synthesis under 200 MPa, the abovementioned white slurry was sealed in the Teflon vessel and then placed in the WIP for the synthesis for 24 h at 100 °C. The high-pressure product was recovered, washed, dried, and calcined as per the same procedure.

Characterization. Powder X-ray diffraction (XRD) patterns of all samples were obtained using a Rigaku Ultima IV diffractometer with Cu Kα radiation (λ = 1.5406 Å, V = 40 kV, I = 40 mA) at a scanning rate of 4° min^{-1}. The product morphology was observed using a field emission scanning electron microscope (FE-SEM, JSM-7000F, JEOL, Japan). Transmission electron microscopy (TEM) images were taken on a JEM-2000EX (JEOL, Japan) under a working voltage of 120 kV. Nitrogen adsorption−desorption isotherms were obtained on a Quantachrome Autosorb-iQ2 instrument at liquid nitrogen temperature with an outgas pretreatment at 325 °C for 4 h under vacuum. Mesopore volume (V_{meso}) was calculated based on the nonlinear density functional theory (NLDFT) method using the adsorption branch of the N_2 adsorption−desorption isotherms.[28,29] Elemental analysis was performed on a Thermo iCAP 6300 inductively coupled plasma-atomic emission spectrometer (ICP-AES). Thermogravimetric and differential thermal analysis (TG−DTA) was conducted on a Rigaku PU 4K from 30 to 800 °C at a heating rate of 10 °C min^{-1} with a flow of 10 vol % O_2 and 90 vol % He mixed gas. The cross-sectional features of the samples were observed using a field emission scanning electron microscope (SU9000, Hitachi). Prior to the observation, the zeolite powders embedded in epoxy resin were cut and polished using a broad Ar^+ ion beam in a cross section polisher (E-3500, Hitachi).

RESULTS AND DISCUSSION

Figure 1A shows the XRD patterns of the pristine USY zeolite and those surfactant-templated at 100 °C for 30 min under different pressures. All of the samples are highly crystalline, even those surfactant-templated at elevated external pressures, as indicated by the XRD patterns. Meanwhile, there was no remarkable change in the Si/Al ratio (Si/Al ratios all around 15) and weight loss after the treatment, which is consistent with the observations in previous studies.[24−26] The bulk morphology of the USY zeolite did not change after the surfactant templating (Figure S3). The crystal lattices of the USY zeolites surfactant-templated under different pressures did not change, as evidenced by the unchanged positions of the XRD peaks shown in Figure 1A. A broad low-angle XRD peak centered at approximately 2° appeared after the treatment, due to the presence of the surfactant-templated mesopores. The surfactant-templated zeolite featured tortuous mesopores, and therefore, the broad peak developed in the low-angle range of

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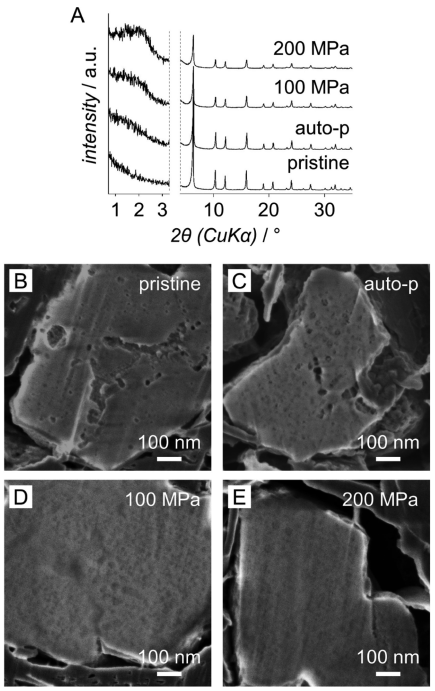

Figure 1. Surfactant templating of the USY zeolite under different pressures. (A) XRD patterns of pristine USY and those surfactant-templated in a CTAB-containing NaOH solution at 100 °C for 30 min under different pressures. (B) Cross-sectional SEM image of pristine USY. (C–E) Cross-sectional SEM images of the USY zeolites surfactant-templated under autogenous pressure, 100, and 200 MPa, respectively.

the XRD pattern.[30] The intensity of this peak increased with the external pressure applied, suggesting that at higher pressures, the mesopores were better ordered. To confirm this point, we examined the cross sections of the samples by a scanning electron microscope (SEM) before and after the treatment. Figure 1B shows that the pristine USY zeolite had large mesopores that were generated by steaming. Figure 1C–E depicts that the evolution from the initially large mesopores to smaller mesopores, which reveals a pressure-dependent tendency. The large mesopores, which were generated by steaming in the manufacture of USY, are the most prevalent after the treatment under autogenous pressure; however, when high external pressure was applied, considerable amounts of smaller mesopores are observed. In particular, the sample surfactant-templated at 200 MPa exhibited the highest amount of smaller mesopores, which is consistent with the XRD patterns shown in Figure 1A. These mesopores were much uniform and of smaller size, which renders the cross section of the surfactant-templated USY to possess fine texture (particularly, as depicted by the SEM image in Figure 1E). This observation was further confirmed by the transmission electron microscopy (TEM) images and by measuring the amount of CTAB occluded in the zeolites (see Figures S4 and S5, respectively, for more details). Collectively considering all these results, we concluded that the surfactant templating of the USY zeolite can be accelerated by applying external pressure.

Figure 2A–C shows the pore size distributions of pristine USY and those surfactant-templated for different periods of time under autogenous pressure, 100, and 200 MPa, respectively. The pore size distributions were derived from the adsorption branch of the N_2 adsorption–desorption isotherms (see Figure S6) at 77 K using a nonlinear density functional theory model (NLDFT model).[28,29] Pristine USY features a low amount of mesopores in the 2–8 nm range (pore width) and a broad pore size distribution. As a result of surfactant templating in the CTAB-containing NaOH solution, the number of mesopores gradually increased with time and the pore size distribution became narrower. These results further confirm that the surfactant templating of USY proceeded much faster under high external pressures than under autogenous pressure. Meanwhile, the pore size distribution of the USY zeolites surfactant-templated under high pressures becomes narrower. Table S1 shows the data of the mesopore volume of the samples, which included only the newly formed mesopores sized in the range of 2–8 nm. The pristine USY zeolite contained mesopores in a broader size distribution, but only a moderate amount of mesoporosity in the range of 2–8 nm. After surfactant templating, uniform mesopores developed apparently, amounting to mesopore volumes higher than 0.35 $cm^3\ g^{-1}$. Again, this result demonstrates that high external pressure prompted pore reconstruction, resulting in a faster increase of uniform mesopores.

As described elsewhere,[24−26] the surfactant-templating process involves the following steps: (1) cleavage of the Si–

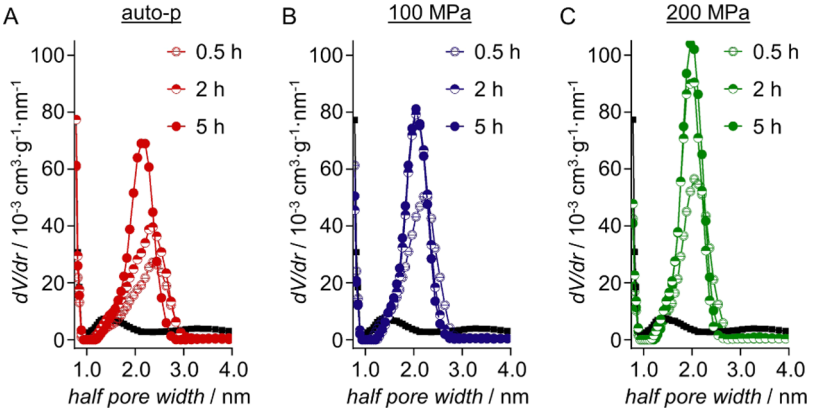

Figure 2. Time evolution of the pore size distributions of the mesoporous USY zeolites surfactant-templated under different pressures. (A–C) Pore size distributions of the USY zeolites treated over different periods of time under autogenous pressure, 100, and 200 MPa, respectively. (The temperature for surfactant templating was 100 °C. The black curve represents the pore size distribution of the pristine USY zeolite.).

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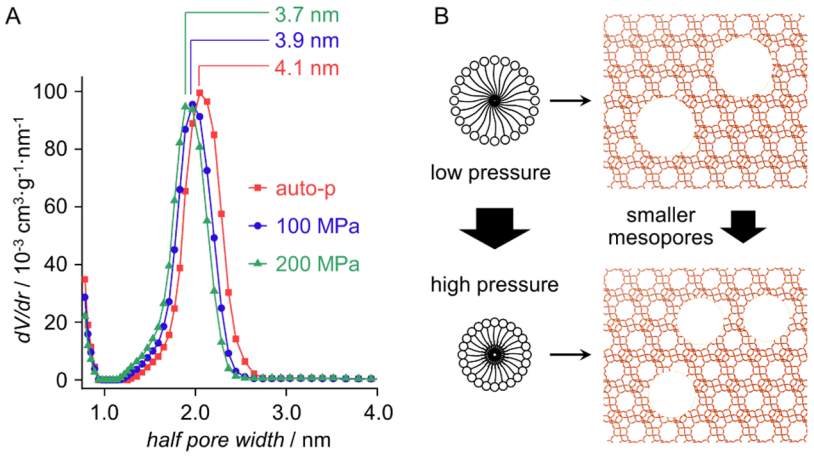

Figure 3. Effect of pressure on the average mesopore size of the surfactant-templated USY zeolite. (A) Comparison of the pore size distributions of the surfactant-templated USY zeolites with CTAB obtained under different pressures. (B) Schematic illustration of the effect of high external pressure on micelle size and corresponding mesopore size. (In all cases, the surfactant templating was performed at 100 °C for 120 h.).

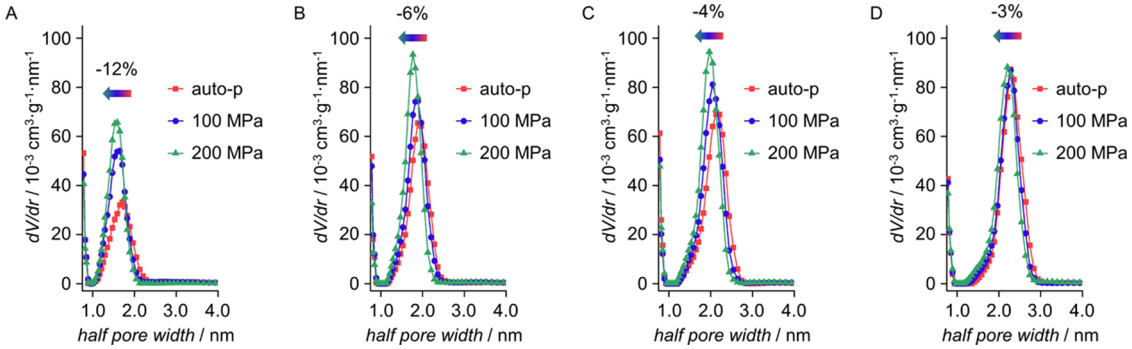

Figure 4. Reduction of mesopore size as a function of external pressure applied during the surfactant templating of the USY zeolite with surfactants of different carbon chain lengths. (A–D) Pore size distributions of the surfactant-templated USY zeolites obtained under different pressures with four trimethylalkylammonium surfactants ($C_nH_{2n+1}N^+(CH_3)_3$, n = 12, 14, 16, and 18, from left to right). (In all of the cases, the surfactant templating was performed at 100 °C for 5 h.).

O–Si bond with the assistance of OH^- ions, which generates abundant Si–O^- sites; (2) admission of CTA^+ cations inside the zeolite driven by the presence of the Si–O^- sites via electrostatic interaction; and (3) formation of well-defined mesopores produced by the micelles that form inside the zeolite where the local concentration of the CTA^+ is high enough. Exerting high pressure on substances in the liquid phase increases their density and reduces the intermolecular distance, which enhances the frequency of collision between molecules.[2,3] Meanwhile, the solubility of electrolytes could be increased in a pressurized aqueous medium.[31,32] As a result of the increased solubility, the external high pressure facilitates the cleavage of the Si–O–Si bonds under the alkaline condition to form the Si–O^- terminal groups, needed for the surfactant templating of the zeolite. In the absence of CTAB, the high-silica zeolite tends to dissolve into the alkaline solution, resulting in structural collapse. Under high pressure, faster dissolution of the USY zeolite was observed, which led to the collapse of its micropore system in just 30 min (Figure S7), an observation that confirms the abovementioned claim of the accelerated cleavage of the Si–O–Si bonds by NaOH under high external pressure. Furthermore, the external high pressure could possibly accelerate the micellization of the CTA^+ inside the USY zeolite, which is a key step in the formation of the smaller mesopores. For the above reasons, we conclude that high external pressure can be used to accelerate the cascade of steps involved in the surfactant templating of the USY zeolite, leading to the faster formation of uniform mesopores. The enhancement of mesopore formation upon high pressure is consistent with our previous study, in which applying high external pressures was found to greatly prompt the crystallization of zeolites from sodium- and potassium-containing aluminosilicate precursors.[17] It is worth noting that the enhancement effect of high external pressure was more pronounced at a higher temperature, as indicated by the results in Figure S8, which is expected due to the role of temperature in overcoming the low activation energy involved in the surfactant templating of the USY zeolite.[25] These results collectively demonstrate that the pressure effect is significant and can be exploited to accelerate the rates of both synthesis and modification of zeolites.

Besides accelerating the rate of surfactant templating, the external high pressure was found to alter the size of the mesopores. Figure 3A compares the pore size distributions of the USY zeolite surfactant-templated under different pressures. The corresponding N_2 adsorption–desorption isotherms are shown in Figure S9. To avoid the influence of synthesis time, the samples were subject to the treatments for enough long period of time (120 h). Under autogenous pressure, an average pore size of 4.10 nm was obtained, which is in accordance with the size of CTAB micelles, as discussed in previous studies.[24–26] In contrast, the average pore sizes for the samples

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treated at 100 and 200 MPa were 3.9 and 3.7 nm, respectively, showing that the mesopores shrunk upon the external high pressures.

A key feature of the surfactant templating of zeolites is that the size of the mesopores is governed by the assembly of the surfactants. The above result suggests that the high external pressure contracts the micelle size of the surfactants, which conveys to the surfactant templating of the USY zeolite and consequently results in a smaller mesopores size (Figure 3B). As CTAB contains long aliphatic chain alkanes, smaller micelles should be expected in a highly pressurized environment, as discussed in previous studies.[33,34]

To further reveal the effect of high external pressure on the assembly of surfactants and thereof the mesopore size of the surfactant-templated USY zeolite, trimethylalkylammonium surfactants with different carbon chain lengths ($C_nH_{2n+1}N^+(CH_3)_3$, n = 12, 14, 16, and 18) were studied. As seen from the results under autogenous pressure (Figure S10), there exists a linear relationship between the carbon number of the alkane chain and the average mesopore size of the surfactant-templated USY zeolite. Figure S11 shows the N_2 adsorption−desorption isotherms of the samples surfactant-templated with surfactants having different carbon chain lengths. Figure 4 shows the comparisons of pore size distributions under different pressures for the four trimethylalkylammonium surfactants. In all cases, the average pore size decreased with pressure. It is worth noting that the smaller the surfactant, the more pronounced the reduction in the mesopore size with pressure. According to previous studies, the number of molecules present in a micelle (known as the aggregation number) is smaller for a surfactant with shorter aliphatic chains.[35,36] A smaller aggregation number also results in a larger void in the micelles, which could explain why the mesopores size reduction at high pressures is more notable for smaller surfactant molecules. On the other hand, smaller surfactants display weaker hydrophobic attraction in the micelle, making its shrinkage more favorable at high external pressures. Table S2 presents average pore sizes and mesopore volumes of the surfactant-templated zeolites under different pressures. In all cases, a high mesopore volume was achieved (>0.25 $cm^3\ g^{-1}$), which indicates that the conditions used were sufficient to surfactant template the zeolite. More importantly, fine control over the mesopore size ranging from ca. 3.2 nm (small surfactant and high pressure) to ca. 4.6 nm (large surfactant and autogenous pressure) was achieved. As many applications of zeolites are enabled via mechanisms of size recognition and spatial confinement, it is particularly important for us to be able to regulate the pore size of zeolites with high precision (in an increase of 0.1 Å) and over a wide spectrum (from the size of small molecules to that of large ones). For example, the separation of ethylene and ethane through molecular sieving requires precise tailoring of the pore size of the porous medium, considering the fact that the kinetic diameters of the two molecules only differ marginally (by 0.28 Å).[6] When bulky reactants or transition states are in a "right fit" with the pores or voids of the zeolite catalysts, the confinement effect can be generated and thus enhance the catalytic performance,[7] which pinpoints the importance of fabricating catalysts with specific size and geometry. These prospects have stimulated considerable efforts in innovating synthesis methods to tailor the pore features of zeolites (and other porous materials). As demonstrated by the above results, the combination of judiciously applying external pressure and appropriately selecting surfactants offered a unique opportunity to tune the mesopore size in the hierarchical USY zeolite with high precision. Thus, we believe that the high-pressure synthesis/modification offers a new method and enriches the toolbox for engineering the pore features of porous materials.

To confirm the impact of high pressure on the shrinkage of the micelles and ultimately on the reduction of the mesopore size of the hierarchical zeolites, we extended our investigation to a well-known surfactant-templated material—mesoporous silica MCM-41. MCM-41 features hexagonally arranged one-dimensional mesopores. It is the best-known and most studied member of the M41S family, a series of ordered mesoporous silica synthesized from quaternary-ammonium-based surfactants.[37,38] Thanks to the extensive knowledge gained over the past few decades, the architecture of the mesopores (hexagonal, cubic, or lamellar) of the M41S materials can be controlled by selecting surfactants of different packing factors (g-factor).[27] Not only the mesopore architecture but also the mesopore size of MCM-41 can be finely tuned by choosing an appropriate surfactant in combination with adopting the right synthesis condition. Because of these features, the synthesis of MCM-41 serves as an excellent model material to study the impact of high pressure on the surfactant templating. Figure 5A

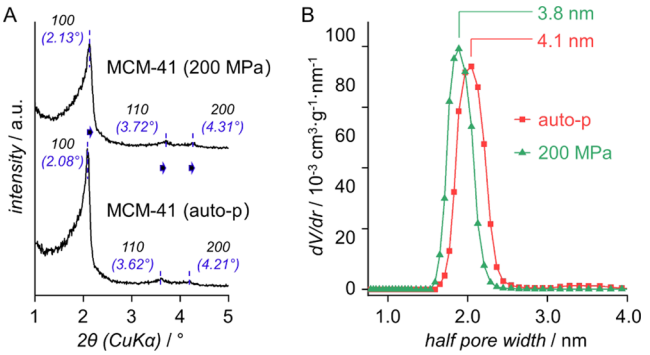

Figure 5. Comparison of the syntheses of MCM-41 under autogenous pressure and 200 MPa. (A) XRD patterns of the MCM-41 samples (the arrows indicate peak shifts toward higher 2θ angles). (B) Pore size distributions of the MCM-41 samples.

shows the XRD patterns of the samples synthesized under autogenous pressure and 200 MPa, from which main reflection lines (d100, d110, and d200) of the hexagonal symmetry of the MCM-41 structure (space group: p6m) are observed.[27] It is worth noting that the high-pressure MCM-41 exhibited XRD peaks that shift to higher 2θ angles compared to the other one, implying that it may contain smaller mesopores. Figure S12 shows the SEM and TEM images of the samples, which together with high Brunauer−Emmett−Teller (BET) surface areas (920 and 880 $m^2\ g^{-1}$ for the samples synthesized under autogenous pressure and 200 MPa, respectively) displayed in Figure S13 further confirm that MCM-41 was successfully synthesized. The pore size distributions calculated from the N_2 adsorption data (Figure 5B) show that the average mesopore size of the high-pressure MCM-41 (3.7 nm) is smaller than that of the one synthesized under autogenous pressure (4.1 nm). This result, significantly consistent with the observations on the surfactant templating of the USY zeolite with CTAB, further validates that high external pressure can be used to affect the self-assembly behaviors of the surfactants and thus alter the pore dimensions of the templated materials. From the

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corresponding d100 reflections in shown Figure 5A, the distances between two mesopore centers in the MCM-41 samples synthesized under autogenous pressure and 200 MPa were calculated to be 4.9 and 4.8 nm, respectively. Thus, the wall thickness was estimated to be 0.8 nm for the autogenous-pressure MCM-41 and 1.1 nm for the high-pressure MCM-41. This result suggests that, along with shrinking the mesopores, high external pressures yield MCM-41 with a thick wall and likely higher structural stability.[39,40]

CONCLUSIONS

In this work, we show how high hydrostatic pressure can be utilized to engineer mesopores in the hierarchical USY zeolite and MCM-41. High external pressure accelerates the cascade of processes responsible for the surfactant templating of the USY zeolite and thus leads to a significantly faster generation of mesopores. Moreover, high external pressure influences the assembly behavior of surfactants; thus, it can be utilized to regulate the micelle size and consequently engineer the mesopore sizes, with subnanometer precision, of the templated USY zeolite and MCM-41. Applying high pressure also yields narrower pore size distributions in templated materials and thickens the pore walls of MCM-41. These results collectively show that high external pressure enriches our toolbox to influence the self-assembly behavior, which is critically important to engineer the porosity of open framework materials. We anticipate that this work will stimulate future studies to exploit the high-pressure synthesis of functional porous materials as well as to gain deeper insights into the processes involved.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.1c02800.

Supporting tables; illustration and photograph of the WIP; N_2 adsorption−desorption isotherms; and SEM and TEM images (PDF)

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Notes

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