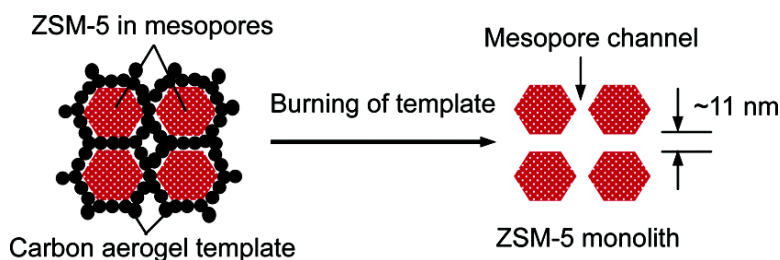


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ZSM-5 Monolith of Uniform Mesoporous Channels

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Zeolites are crystalline porous solids with intricate pore and channel systems in the molecular size range of 0.3 to ~1.5 nm. They are widely used in industry as heterogeneous catalysts and are particularly used in the fields of oil refining and petrochemistry as solid acid catalysts.¹ Although the micropores of zeolite have been well described as having excellent potential for chemical functions, diffusion in the micropores often intervenes the chemical process, because the micropores often impose diffusion limits on the reaction rate.² A controlled reduction of the zeolite's crystal size has been attempted as a means to solve this micropore diffusion problem.³ However, none of these attempts have produced an easy means of controlling the crystal size. Moreover, filtration of the small zeolite crystals is difficult due to the colloidal properties of these materials. If we could donate uniform mesopores to zeolites, the resulting bimodal pore-structured zeolites would further extend the applications of zeolites, since this would combine the benefits of both pore-size regimes. For example, micropores in zeolites provide size- or shape selectivity for guest molecules, while mesopores provide easier access to the active sites in micropores. Recently, Jacobsen et al.⁴ prepared mesoporous ZSM-5 of a wide pore size distribution of 10–100 nm by impregnating them with carbon black particles, and Holland et al.⁵ synthesized macroporous (average diameter: 250 nm) silicates by using arrays of monodisperse polystyrene (PS) spheres as templates.

Here we report a unique method of preparing zeolite ZSM-5 monolith with a bimodal pore structure of uniform mesopores (average diameter: 11 nm) by the templating method using a carbon aerogel of uniform mesopores. Carbon aerogel is known to have uniform mesopores and is obtainable in a monolithic form.⁶

For the synthesis of ZSM-5, the established procedures were followed;⁷ so-called clear aluminosilicate solutions were prepared from tetraethyl orthosilicate (TEOS) and aluminum isopropoxide [Al(*i*-PrO)₃], and NaOH, H₂O, and tetrapropylammonium bromide (TPABr) with composition (molar basis) 10 Na₂O:200 SiO₂:Al₂O₃:20 TPABr:16000 H₂O. The synthesis of the ZSM-5 monolith of mesopores (meso-ZSM-5) consisted of three steps: (1) Introducing the zeolite precursor into the mesopores of carbon aerogel, which has a designed diameter of 23 nm. The carbon aerogel was prepared using the Pekala method.⁶ Briefly, resorcinol–formaldehyde (RF) gels were derived from the sol–gel polymerization of resorcinol and formaldehyde with a slight amount of sodium carbonate as a basic catalyst. The molar ratio of resorcinol to catalyst was 200. The RF aerogels were dried under a supercritical condition with CO₂, followed by pyrolysis under N₂ flow at 1323 K. The resultant carbon aerogel was then obtained in the form of vitreous black monoliths. (2) Synthesizing zeolite ZSM-5 in the inert mesopores of the carbon aerogel. The conditions employed were similar to those used in the synthesis of ZSM-5. (3) Separating the zeolite crystals from carbon aerogel. After the synthesis, the products were

washed with distilled water, dried in air at 383 K, and finally heated in O₂ diluted with Ar at 823 K for 18 h to ensure complete combustion of the carbon material, as well as to remove any organics. The principle of the synthesis scheme is shown schematically in Figure 1.

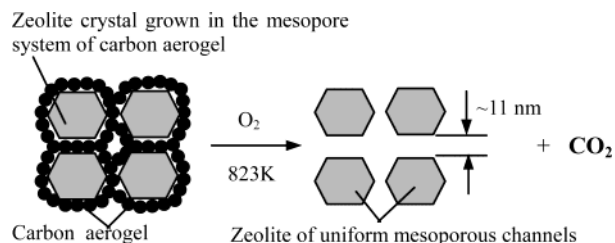


Figure 1. Growth of zeolite crystals in uniform mesopores of carbon aerogel consisting of interconnected uniform carbon particles. The mesopores are large enough to allow the gel to be sufficiently concentrated and to allow growth to continue until the mesopores are filled.

The X-ray diffraction pattern of ZSM-5 coincides with that reported in the literature,^{7,8} and the X-ray diffraction of meso-ZSM-5 also agrees with that of conventional ZSM-5, as is shown in Figure 2, with no evidence of other crystalline phases. However, the crystallite size of meso-ZSM-5 is smaller than that of ZSM-5 due to slight line broadening of the diffraction peaks.

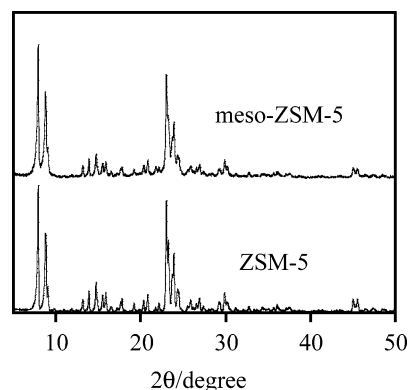


Figure 2. XRD patterns of ZSM-5 and meso-ZSM-5 powders.

For both ZSM-5 and meso-ZSM-5, in the IR spectrum of the framework absorption region (1500–300 cm⁻¹), absorption bands were observed at 1224, 1150–1050, 795, 550, and 455 cm⁻¹. The spectra of the samples of ZSM-5 and meso-ZSM-5 were identical, with respect not only to band positions but also to peak intensity. Absorption bands at 1224 cm⁻¹ (external asymmetric stretch), 1150–1050 cm⁻¹ (internal asymmetric stretch), 795 cm⁻¹ (external symmetric stretch), and 455 cm⁻¹ (T–O bend) are typical for highly siliceous materials,⁹ while the framework vibration at 550 cm⁻¹ (double ring) is characteristic of MFI-type zeolites.¹⁰ The optical density ratio of the 550 and 450 cm⁻¹ bands for ZSM-5 was 0.81,

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and that for meso-ZSM-5 was 0.80. Results of the previously mentioned vibration examination showed that even the meso-ZSM-5 displayed a good crystalline frame structure, as the optical density ratio of all pure pentasil samples in the literature is 0.8.¹¹

Figure 3 is a field emission scanning electron micrograph (FE-SEM) of the synthesized meso-ZSM-5 monolith. The average size of the monolith is 3–5 mm (inset). Uniform mesopores of ca. 10 nm in width can be seen in the interspherical particles shown in the magnified image.

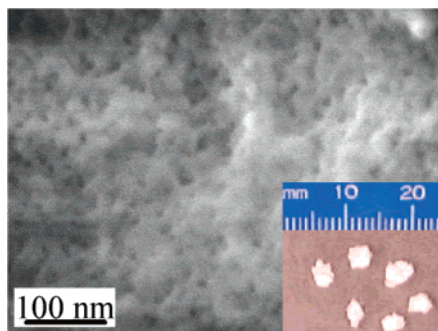


Figure 3. Field emission scanning electron micrograph of the meso-ZSM-5 crystals and photograph of meso-ZSM-5 monolith (inset).

The N₂ adsorption isotherm of carbon aerogel used as a template has a clear type-H1 hysteresis loop with almost vertical adsorption and desorption branches, which comes from an agglomerate structure of uniform spherical particles. The adsorption hysteresis of N₂ adsorption isotherm and the FE-SEM showed that the mesopores are quite uniform. SPE analysis and the Dollimore–Heal (DH) method of the N₂ adsorption isotherm showed that the surface area was 1330 m² g⁻¹, mesopore volume was 3.15 cm³ g⁻¹, (the micropore volume was 0.19 cm³ g⁻¹), and mesopore size was 23 nm. Accordingly, a carbon aerogel monolith can supply nanostructures suitable for template synthesis. Figure 4 shows the N₂ adsorption isotherm of ZSM-5 and that of meso-ZSM-5 at 77 K. The N₂ adsorption isotherm of ZSM-5 basically belongs to IUPAC type I, as indicated by the literature.¹² The predominant adsorption finishes below $P/P_0 = 0.02$, which is a characteristic of uniform microporous solids. The N₂ adsorption isotherm of meso-

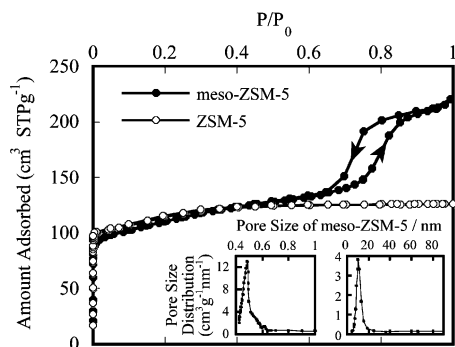


Figure 4. Adsorption/desorption isotherms of nitrogen at 77 K on ZSM-5 (○) and meso-ZSM-5 (●). Inserts show Saito–Foley micropore and DH mesopore size distributions of meso-ZSM-5.

ZSM-5, as expected to have a much larger adsorption amount than that of ZSM-5, has a steep uptake below $P/P_0 = 0.02$ and a hysteresis loop above $P/P_0 = 0.6$. Thus, the co-presence of micropores and mesopores is suggested by the N₂ adsorption isotherm. The size distribution of the mesopores is shown in the inset of Figure 4. The pore size distribution is very narrow with a maximum at ca. 11 nm and a width at half-height of only ca. 3 nm. The Saito–Foley method was used to analyze the ZSM-5 and meso-ZSM-5 micropores. The micropores of both ZSM-5 and meso-ZSM-5 were 0.51 nm in size (the micropore size distribution of meso-ZSM-5 shown in the inset in Figure 4). This size is comparable to the free diameter of a crystallographic 10-membered-oxygen ring. The parameters for the pore structure are given in Table 1.

Table 1. Pore Structural Parameters of Meso-ZSM-5 and ZSM-5

	S_{BET} (m ² g ⁻¹)	micropore vol (cm ³ g ⁻¹)	meso-pore vol (cm ³ g ⁻¹)	meso-pore diam (nm)	micropore diam (nm)
meso-ZSM-5	385	0.15	0.2	11 ± 2	0.51
ZSM-5	395	0.17			0.51

In summary, a highly crystalline meso-ZSM-5 monolith was synthesized that has the crystalline form of ZSM-5 with both micropores and mesopores. Using a template of carbon aerogel to donate uniform mesopores to zeolites should remarkably extend their applications because the additional uniform mesopores lead to easier access to the active sites. Detailed studies of the sorption behavior and catalytic reactivity are currently underway.

Acknowledgment. Support of this work by New Energy and Industrial Technology Development Organization of Japan (NEDO) is gratefully acknowledged.

Supporting Information Available: Details of the synthesis and FT-IR spectrum of meso-ZSM-5 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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