

MESOPOROUS ZEOLITES FROM CARBON AEROGEL TEMPLATING

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Introduction

Recently many nanoporous carbons have been synthesized using templating method. On the contrary, carbons can be applied as the template, because carbon can be gasified. Zeolite molecular sieves are crystalline porous solids with intricate pore and channel systems in the molecular size range of 0.3 to ~3 nm. They are widely used in industry as heterogeneous catalysts [1]. Although micropores of zeolite are uniform, diffusion in the micropores often intervenes the chemical process [2]. A controlled reduction of the zeolite's crystal size has been attempted as a means to solve this micropore diffusion problem [3]. However, such attempts are not necessarily successful. If we could donate uniform mesopores to zeolites, the resulting bimodal pore-structured zeolites would further extend the applications of zeolites. Recently, Jacobsen et al [4]. prepared mesoporous ZSM-5 of a wide pore size distribution of 10 to 100 nm by impregnating them with carbon black particles, and Holland et al.⁵ synthesized macroporous (250 nm average diameter) silicates by using arrays of monodisperse polystyrene (PS) spheres as templates.

We prepared zeolite ZSM-5 monolith with a bimodal pore structure of uniform mesopores (11 nm average width) by the templating method using a carbon aerogel of uniform mesopores. Carbon aerogel is well known to have uniform mesopores [6].

Experimental

For the synthesis of ZSM-5, the established procedures were followed [7]. 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. (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 and drying, the

products were 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.

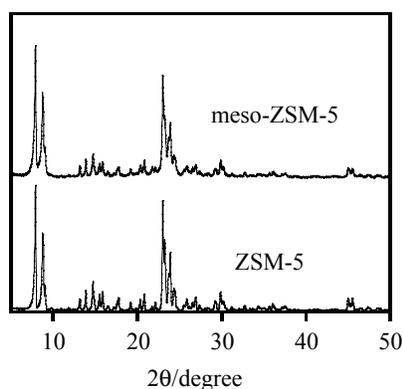


Figure 1. XRD patterns of ZSM-5 and meso-ZSM-5

Results and Discussion

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 1, with no evidence of other crystalline phases. Also the IR spectroscopic examination supported the formation of well crystalline ZSM-5 in mesopores of carbon aerogels. Figure 2 is a field emission scanning electron micrograph (FE-SEM) of the synthesized meso-ZSM-5 monolith. The average length of the monolith is 3-5 mm (inset). Uniform mesopores of ca. 10 nm in width can be seen in the inter-spherical particles shown in the magnified image.

The N₂ adsorption isotherm of carbon aerogel used as a template has a clear type-H1 hysteresis loop, which comes from an agglomerate structure of uniform spherical particles. The adsorption hysteresis of N₂ adsorption isotherm and the FE-SEM showed that the presence of uniform mesopores. Analysis 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 be suitable for template synthesis. Figure 3 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. The predominant adsorption finishes below P/P₀ = 0.02, which is a characteristic of uniform microporous solids. The N₂ adsorption isotherm of meso-ZSM-5, as expected to have a much larger adsorption amount than that of ZSM-5, has a steep uptake below P/P₀ = 0.02 and a hysteresis loop above P/P₀ = 0.6. Thus, the co-presence of micropores and mesopores is elucidated by the N₂ adsorption isotherm. 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 micropores of both ZSM-5 and meso-ZSM-5 were 0.51 nm in size. 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.

In the similar way, we can synthesize meso-NaA and meso-NaY. These results will be also presented.

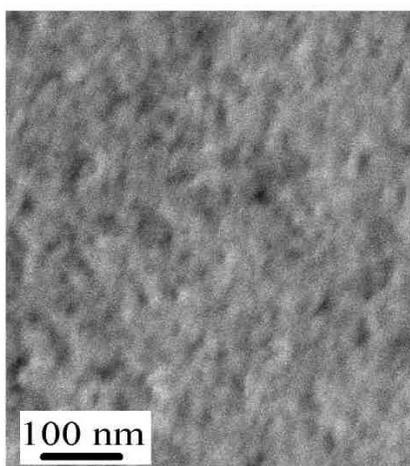


Figure 2. Field emission scanning electron micrograph of the meso-ZSM-5 crystals

Table 1. Pore structural parameters of meso-ZSM-5 and ZSM-5

	S_{BET} (m^2g^{-1})	micro-pore vol. (cm^3g^{-1})	meso-pore vol. (cm^3g^{-1})	meso-pore size (nm)	micro-pore size (nm)
meso-ZSM-5	385	0.15	0.2	11±2	0.51
ZSM-5	395	0.17	-	-	0.51

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