Uniform Mesopore-Donated Zeolite Y Using Carbon Aerogel Templating

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Zeolite Y of mesoporous channels has been synthesized using novel mesoporous carbon aerogels as template. It was characterized with X-ray powder diffraction, Fourier transform infrared spectroscopy, field emission scanning electron microscopy (FE-SEM), thermogravimetric analysis, and nitrogen adsorption/desorption. The pore size distribution with N_2 adsorption shows the presence of mesopores and micropores whose average pore widths are ca. 10 and 0.75 nm, and pore volumes are 1.37 and 0.21 cm^3 g^{-1}, respectively. FE-SEM observation supports the presence of mesopores.

Introduction

Zeolite Y with the faujasite (FAU) framework is a highly versatile molecular sieve and has been extensively used as a component of fluid catalytic cracking (FCC) catalysts for refining oil and as a material for adsorbing and removing gaseous emissions.[1−3] In recent years, its application has been expanded to biochemistry as an adsorbent matrix in the purification of proteins.[4] The micropore structure of zeolite originates from the intrinsic crystalline structure. Although the intrinsic micropores have excellent potential for chemical functions, in many applications, the intricate pore and channel systems in the molecular size range impose diffusional limitations on the reaction rate as well as a high backpressure on flow systems.[5] In the case of heterogeneous catalysis, fast mass transfer of the reactants and products to and from the catalytic sites is required and thereby mesopore-structured zeolites are of great interest. Up to now, a subsequent hydrothermal dealumination treatment of zeolite Y has been attempted; defect domains of 5−50 nm in size which are attributed to mesopores have been produced. However, this treatment cannot provide zeolite Y of having uniform mesopores in size and lattice position. Such inhomogenities are even more pronounced for a higher temperature stream-deactivated commercial USY cracking catalyst.[6−8]

Carbon aerogels are known to have uniform mesopores and is obtainable in a monolithic form.[9,10] Moreover, the pore-controlled carbon aerogels could be tailor-made by design.[10] These authors succeeded in preparation of well-crystalline ZSM-5 having uniform mesopores using carbon aerogels as the template.[11] This letter reports that the template route using carbon aerogels can provide zeolite Y of uniform mesopore channels.

Experimental Section

The agents used for synthesis of zeolite Y were aluminum isopropoxide (Al(^{i}PrO)$_3$, minimum 95.0%, Wako), silica sol (SiO$_2$, 30%, Aldrich), tetramethylammonium hydroxide pentahydrate (TMAOH·5H$_2$O, ICN), and sodium hydroxide pellets (NaOH, minimum 96.0%, Wako). Resorcinol (C$_6$H$_4$(OH)$_2$, minimum 99.0%, Wako), formaldehyde solution (HCHO, 36.0−38.0%, Wako), sodium carbonate (Na$_2$CO$_3$, minimum 99.5%, Wako), and trifluoroacetic acid (CF$_3$COOH, minimum 98.0%, Wako) were used for synthesis of carbon aerogel template. First, the carbon aerogel template was prepared using the Pekala method.[9,10] 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 (R) to catalyst (C) was held at R/C = 200. The RF aerogels were dried with supercritical CO$_2$, followed by pyrolysis under N$_2$ flow at 1323 K. The resultant carbon aerogel was then obtained in the form of vitreous black monoliths. The synthesis of zeolite Y (NaY) used as the standard in this study was performed from a clear aqueous solution with a mole composition of 1.00Al$_2$O$_3$:4.35SiO$_2$:2.39(TMA)$_2$O:0.065Na$_2$O:248.00H$_2$O at 373 K. For the synthesis of zeolite Y of mesoporous channels (*meso*-NaY), a reaction mixture with the same composition as that for the synthesis of zeolite Y was transferred to a reaction cell containing carbon aerogel template, which was evacuated at 383 K and 1 mPa for 2 h prior to use; the zeolite precursor was introduced into the mesopores of carbon aerogels. Then the reaction cell was transferred into a stainless steel autoclave and heated in an oven at 373 K for 216 h. After the hydrothermal synthesis the monolithic carbon aerogels containing zeolites were separated. The carbon aerogel template was removed by firing in an oxygen flow at 803 K for 18 h after washing and drying. Finally the *meso*-NaY was obtained. Several runs of the sample preparation were done with reproducible results.

The powder X-ray diffraction (XRD) patterns were acquired on a M18XHF X-ray automatic diffractometer (MacScience Co.) using a monochromatized X-ray beam from nickel-filtered Cu Kα (0.154050 nm) radiation. The Fourier transform infrared (FT-IR) absorption spectra in the zeolite framework vibration region were obtained with FT/IR-410 spectrometer (JASCO Co.) using the KBr pellet technique. Spectrum was acquired in a wavenumber range between 400 and 1500 cm^{-1} at 2 cm^{-1} resolution. The field emission scanning electron microgragh of the samples was obtained on a JEOL JSM-6330F scanning electron microscope without Au sputtering. The thermogravimetric analysis (TGA) of the samples was performed on SII,

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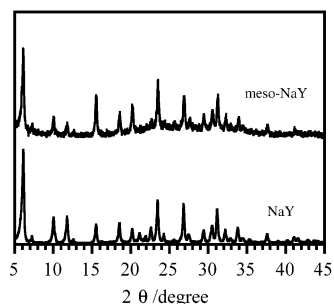‡ Center for Frontier Electronics and Photonics, Chiba University.

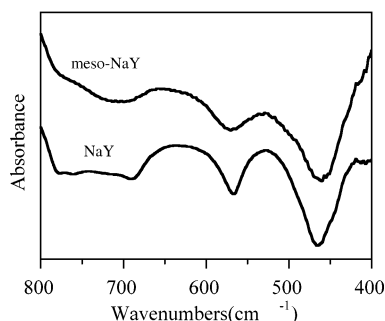**Figure 1.** XRD patterns of *meso*-NaY and NaY.

Figure 2. FTIR spectra of *meso*-NaY and NaY in the region of low wavenumbers between 400 and 800 cm^{-1}.

TG/DTA 6200 up to 1273 K at a heating rate of 1 K/min in a mixture flow of oxygen and nitrogen of 200 mL/min. The nitrogen adsorption isotherms were measured at 77 K using a gas sorption analyzer (Quantachrome Autosorb-1). The carbon aerogels were degassed at 383 K for 2 h and both NaY and *meso*-NaY were degassed at 623 K for 12 h under a vacuum of 10^{-4} Pa prior to the adsorption measurement.

Results and Discussion

Figure 1 shows X-ray powder diffraction patterns of *meso*-NaY and NaY. The *meso*-NaY has the characteristic XRD peaks of NaY, and both the XRD patterns match very well with the simulated XRD powder pattern for FAU zeolite.[12] Hence, the XRD data indicates that *meso*-NaY crystals are pure FAU zeolite with high crystallinity. The average crystallite size of *meso*-NaY is calculated to be ca. 80 nm for the diffraction peaks at 2θ values of 6° [111], 10° [220], 16° [331], and 24° [533] using the Scherrer equation.[13]

The *meso*-NaY was further characterized by FT-IR spectroscopy, as shown in Figure 2. The IR spectra of *meso*-NaY and NaY samples contain bands at 570 and 470 cm^{-1}. The band at 470 cm^{-1} is assigned to structure-insensitive T−O bending modes for tetrahedral TO$_4$ units (T = Si or Al), while the band at 570 cm^{-1} is attributed to the double ring external linkage peak associated with the FAU structure. The FT-IR spectra coincide well with the characteristic zeolite Y absorption peaks laid out in the literature.[14,15]

Figure 3 shows the typical scanning electron microscopic images of *meso*-NaY and carbon aerogel template. The image of carbon aerogel of high electrical conductivity is much clearer than that of insulative *meso*-NaY. Mesopores with an average size of ca. 20 nm and walls with uniform size of ca. 10 nm between the mesopores are very well-defined for the carbon aerogel template[9,10] (Figure 3B). Mesopores develop three-dimensionally in the monolith of carbon aerogel. The dim picture of *meso*-NaY cannot directly give the evidence for copying the carbon aerogel structure. However, the presence of mesoporous channels with dimension ca. 10 nm is still observed (Figure
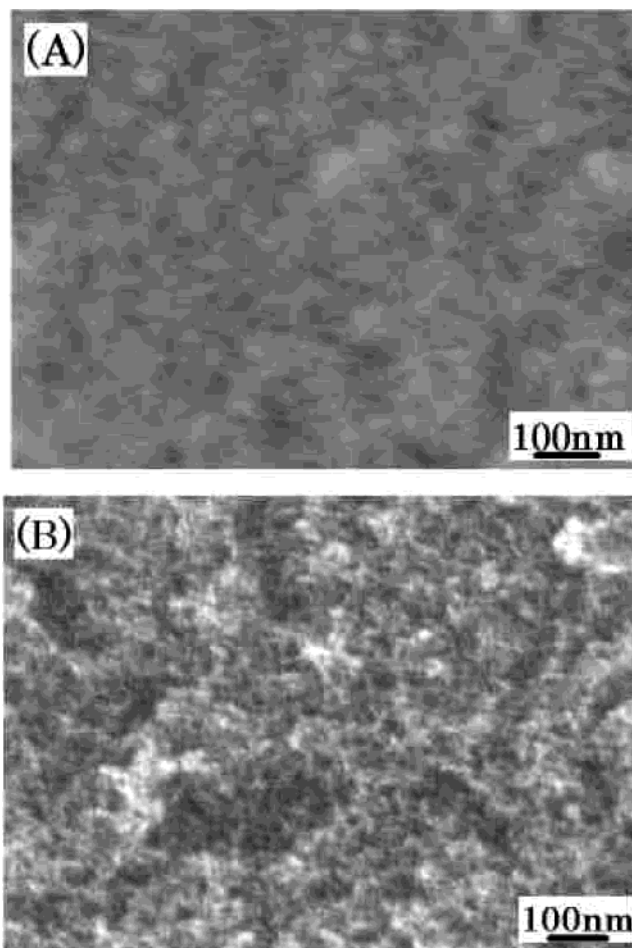

Figure 3. Field emission scanning electron microscopic images of (A) *meso*-NaY and (B) carbon aerogels.

3A). We can say that the mesopore structure of *meso*-NaY copies the framestructure of the carbon aerogel template.

TGA of the zeolite/carbon aerogel composite showed that most of the weight loss occurred between 733 and 803 K in a mixture flow of oxygen and nitrogen, corresponding to the removal of carbon in the composite. At a temperature lower than 733 K, a slight weight loss of the composite is ascribed to water desorption and decomposition or volatilization of TMA. This confirms that no carbon aeogel template is left in the *meso*-NaY samples. The obtained residue after heating above 803 K was weighted to be only 6−8% of the initial composite, indicating the donating of high pore volume to the products by means of the carbon aerogel template.

Adsorption/desorption isotherms of N$_2$ (77 K) on the carbon aerogel template have a clear hysteresis loop of type H1, which stems from agglomerates of uniform spherical carbon particles. As the adsorption and desorption branches of the loop are almost vertical, the mesopores are quite uniform. SPE analysis and the Dollimore−Heal (DH) method of the N$_2$ adsorption isotherm showed that the surface area was 1330 m^2 g^{-1}, mesopore volume was 3.15 cm^3 g^{-1} (the micropore volume was 0.19 cm^3 g^{-1}), and mesopore size was 23 nm. Accordingly, a carbon aerogel monolith can supply uniform nanopore structures suitable for the template synthesis. Typical nitrogen adsorption/desorption isotherms of *meso*-NaY and NaY are shown in Figure 4. Distinct differences between *meso*-NaY and NaY in the shapes of the isotherms are observed. The adsorption isotherm of NaY is of typical type I, which is generally observed for microporous solids. The isotherm of *meso*-NaY exhibits type IV behavior,
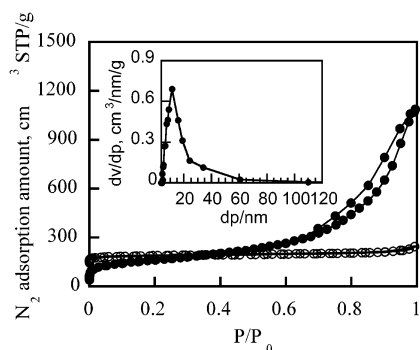
Figure 4. Adsorption/desorption isotherms of nitrogen at 77 K on *meso*-NaY(●) and NaY(○). Inset shows DH mesopore size distribution of *meso*-NaY.

displaying a hysteresis loop above $P/P_0 = 0.6$, which arises from additional pores brought by the removal of the carbon aerogel template. The additional pores are supported by the above scanning microscopic image in Figure 3A. Moreover *meso*-NaY, as expected, results in much larger N_2 adsorption amount than NaY does due to a significant increase in the porosity. The ratio of N_2 adsorption amount of *meso*-NaY to NaY at $P/P_0 = 0.98$ is 4.5. The steep uptakes in N_2 adsorption isotherms of both *meso*-NaY and NaY below $P/P_0 = 0.02$ indicate complete filling of uniform micropores. Dollimore–Heal (DH) method and Saito–Foly method were used to determine the mesopore size distribution of *meso*-NaY and the micropore size distributions of both *meso*-NaY and NaY, respectively. The mesopore size distribution (PSD) of *meso*-NaY is presented in the inset of Figure 4. According to the PSDs of samples, the pore volume of NaY is attributed to micropores and the PSD peak is at 0.75 nm. The pore volume of *meso*-NaY originates from both micropores and mesopores, and the PSD peaks are at 0.75 and 10 nm. The peak positions of both *meso*-NaY and NaY in the micropore PSDs agree with each other, which are close to the free aperture of main channels of zeolite Y.[14,16] The mesopore PSD of *meso*-NaY is sharp and has a peak at 10 nm, which almost corresponds to the thickness of the pore wall of carbon aerogel template, as shown in the scanning electron microscopic image of carbon aerogels (Figure 3B). The pore structural parameters derived from the nitrogen adsorption/desorption isotherms are summarized in Table 1.

In conclusion, a highly crystalline zeolite Y of mesoporous channels has been synthesized with the template method using a novel mesoporous template of carbon aerogel. The *meso*-NaY has the FAU framework with relatively uniform mesoporous

TABLE 1: Surface Areas and Porosity Data for *meso*-NaY and NaY

	S_{BET} (m^2 g^{-1})	micropore vol (cm^3 g^{-1})	mesopore vol (cm^3 g^{-1})	mesopore width (nm)	micropore width (nm)
meso-NaY	581	0.21	1.37	10	0.75
NaY	646	0.29			0.75

channels and the additional mesopore volume is as high as 1.37 cm^3 g^{-1}. It is expected that the mesoporous interchannels provide greater accessibility to the micropores intrinsic to the zeolite crystal structure. The mesopore structure of carbon aerogels can be varied by the chemical conditions,[10] and thereby, the mesoporous structure of the finally obtained zeolite can thus be controlled by a proper preparation method of carbon aerogel template.

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