Electronic Supplementary Information for

Hydrophobic Zeolites Coated with Microporous Organic Polymer: Adsorption Behavior of Ammonia under Humid Conditions

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Experimental Sections

SEM images were obtained using a FE-SEM (JSM6700F). TEM images were obtained using a JEOL 2100F instrument. N_2 sorption isotherms (77 K) were measured using a BELSORP II-mini equipment. For the pore size analysis, the DFT method was applied. PXRD patterns were obtained using a Rigaku MAX-2200 operating with filtered Cu-Ka radiation. Solid phase ^{13}C-NMR spectra were obtained on a Bruker 400 MHz Solid State DSX NMR spectrometer at the Korea Basic Science Institute (Daegu, South Korea). Elemental analysis was performed using a CE EA1110 elemental analyzer. Water contact angles of pellet samples were measured using the Theta Optical Tensiometer model (KSV instruments, Ltd.) and electrooptics comprising a CCTV camera connected to a computer (software Attension Theta).

Synthetic procedure for ZSM-5 particles

ZSM-5 nanoparticles were prepared by the procedures in the literature. (Y. –P. Guo, T. Long, Z. –F. Song, Z. –A. Zhu, *J. Biomed. Mater. Res. B: Appl. Biomater.* 2014, *102*, 583-891.) Tetraethyl orthosilicate (9.8 mL, 0.044 mol), aluminum isopropoxide (0.010 g, 0.049 mmol), tetrapropyl ammonium hydroxide (8.45 mL, 1.0 M aqueous solution), and water (13 mL) were added to a 100 mL Schlenk flask. The reaction mixture was heated at 90^{o}C for 20 hours. 3-Aminopropyl trimethoxysilane (0.39 mL, 0.022 mol) was added. The reaction mixture was heated at 90^{o}C for 6 hours. The solution was transferred to autoclave and heated at 170^{o}C for 5 days. After cooling to room temperature, the zeolite particles were retrieved by centrifugation, washed with distilled water (40 mL) five times, and dried under vacuum at 110^{o}C for 12 hours. In furnace, the powder was treated at 550^{o}C for 4 hours in air.

Synthetic procedure for ZSM-5@MOP

For the synthesis of ZSM-5@MOP-2, ZSM-5 (0.20 g), $(PPh_3)_2PdCl_2$ (3.4 mg, 4.8 μmol) and CuI (1.0 mg, 5.3 μmol) were added to a mixture of toluene (20 mL) and triethylamine (10 mL) in a vial. The reaction mixture was sonicated for 1 hour. The mixture was transferred to a 50 mL Schlenk flask and heated at 70^{o}C for 3 hours under argon. Tetrakis(4-ethynylphenyl)methane (20 mg, 0.048 mmol) and 1,4-diiodobenzene (32 mg, 0.096 mmol) were added. The reaction mixture was heated at 90^{o}C for 24 hours. After cooling to room temperature, the powder was retrieved by centrifugation, washed with MeOH (20 mL, three times) and acetone (20 mL, three times), and dried under vacuum. For the synthesis of ZSM-5@MOP-1, tetrakis(4-ethynylphenyl)methane (10 mg, 0.024 mmol) and 1,4-diiodobenzene (16 mg, 0.048 mmol) was used with same procedure as ZSM-5@MOP-2. For the synthesis of ZSM-5@MOP-3, $(PPh_3)_2PdCl_2$ (6.8 mg, 9.6 μmol), CuI (2.0 mg, 10 μmol), tetrakis(4-ethynylphenyl)methane (40 mg, 0.096 mmol), and 1,4-diiodobenzene (63 mg, 0.19 mmol) was used with same procedure as ZSM-5@MOP-2.

Synthetic procedure for hollow MOP materials

In a 50 mL Falcon tube, ZSM@MOP was dispersed in a mixture of methanol (15 mL) and water (15 mL). HF solution (50% aqueous solution, 10 mL) was added. *Caution: The HF solution is extremely dangerous and needs special care.* The reaction mixture was stirred for 1 hour at room temperature. The powder was retrieved by centrifugation, washed with water (40 mL, five times), methanol (40 mL, three times), and acetone (40 mL, three times), and dried under vacuum

Adsorption tests

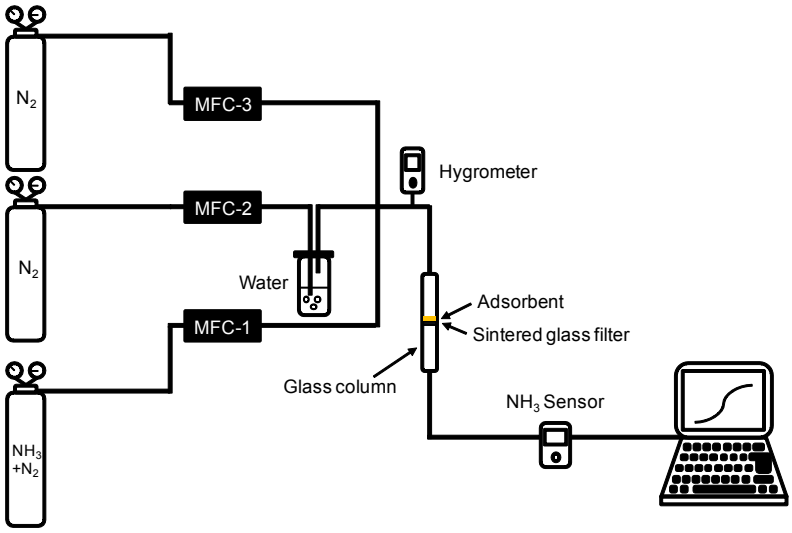

Figure above shows the set-up for adsorption tests conducted at 20°C. The adsorbents were loaded on a sintered glass filter (G3 pore size, 0.8 cm diameter) in a glass column (30 cm × 1 cm). When 50 mg of zeolite and ZSM-5@MOP-2 were loaded, the loading height was 0.3 cm and 0.5 cm, respectively. When 300 mg of zeolite was loaded, the loading height was 1.6 cm. Using a mass flow controller (MFC), NH_3 in N_2 was passed with a fixed 3.4 sccm flow rate for all the tests. The humidity of the system was controlled using additional two MFCs which controlled the flow rates of the wet N_2 flow and the dry N_2 flow, respectively. The relative humidity (RH) was measured by HT-3009 hygrometer (Lutron electronic). For the dry condition, dry N_2 was applied with a 40 sccm flow rate. For the 10% RH, dry N_2 with a 35 sccm flow rate and wet N_2 with a 5 sccm flow rate were applied. For the 43% RH, dry N_2 with a 20 sccm flow rate and wet N_2 with a 20 sccm flow rate were applied. For the 76% RH, dry N_2 with a 5 sccm flow rate and wet N_2 with a 35 sccm flow rate were applied. The wet N_2 flow was prepared by mixing of water vapour (prepared by water bubbling) with N_2 flow. (See the following figure.) For all the tests, the total flow rate was fixed as 43.4 sccm. The inlet concentration of ammonia for adsorbents was 4500 ppm, which was obtained by calibration plot. The outlet NH_3 concentration was measured by Gasman-NH_3 sensor (Crowcon Co.). The upper detection limit of the ammonia sensor was 1000 ppm. Thus, we stopped the measurement at 900 ppm. The breakthrough time was measured at 450 ppm NH_3 outlet concentration. The breakthrough capacities (mg NH_3/g) were calculated using breakthrough times, inlet concentration, flow rate values, and mass of adsorbents.

Fig. S1 SEM image of the ZSM-5 nanoparticles used in this study.

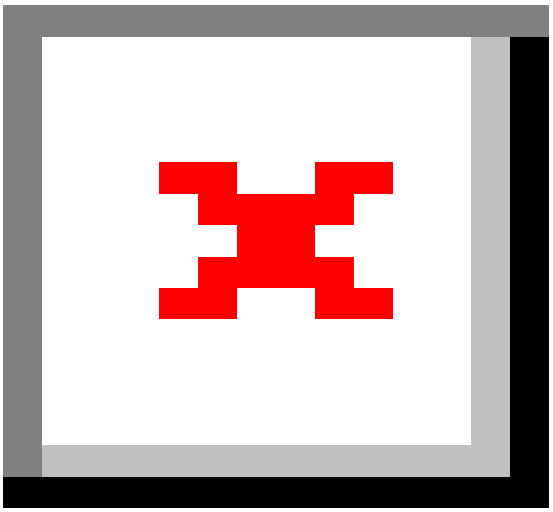

Fig. S2 SEM images of the ZSM-5@MOP materials.

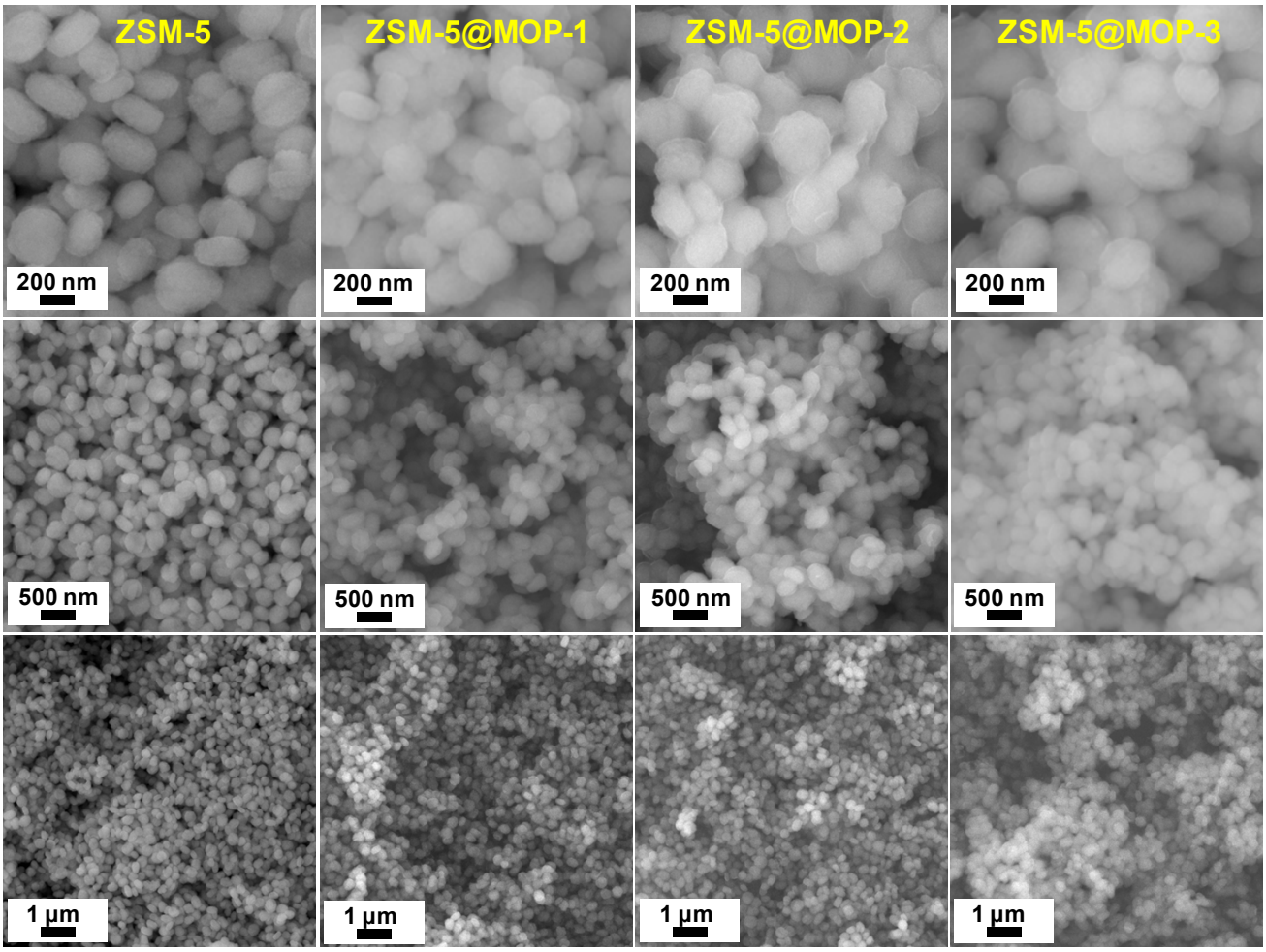

Fig. S3 Solid phase ^{13}C NMR spectra of ZSM-5@MOP-1, ZSM-5@MOP-2, and ZSM-5@MOP-3.

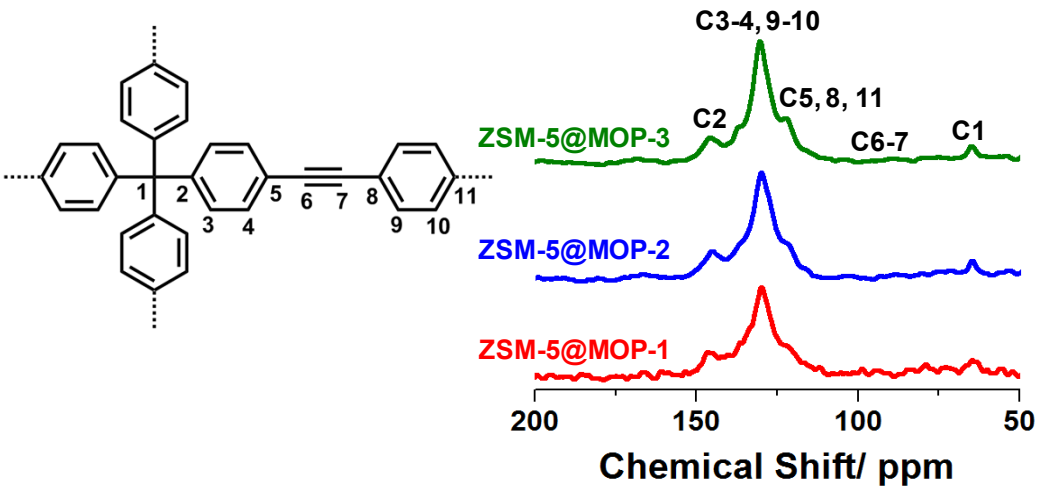

Fig. S4 (a) NH_3 adsorption behavior of the ZSM-5@MOP-2 and the recovered ZSM-5@MOP-2 at 43% RH. The retrieved ZSM-5@MOP-2 was dried under vacuum at 120 °C for 12 hours for the next runs. (b) NH_3 adsorption behavior of hollow MOP materials under dry conditions. (c) Characterization data of hollow MOP-2 obtained by ZSM-5 etching of ZSM-5@MOP-2.

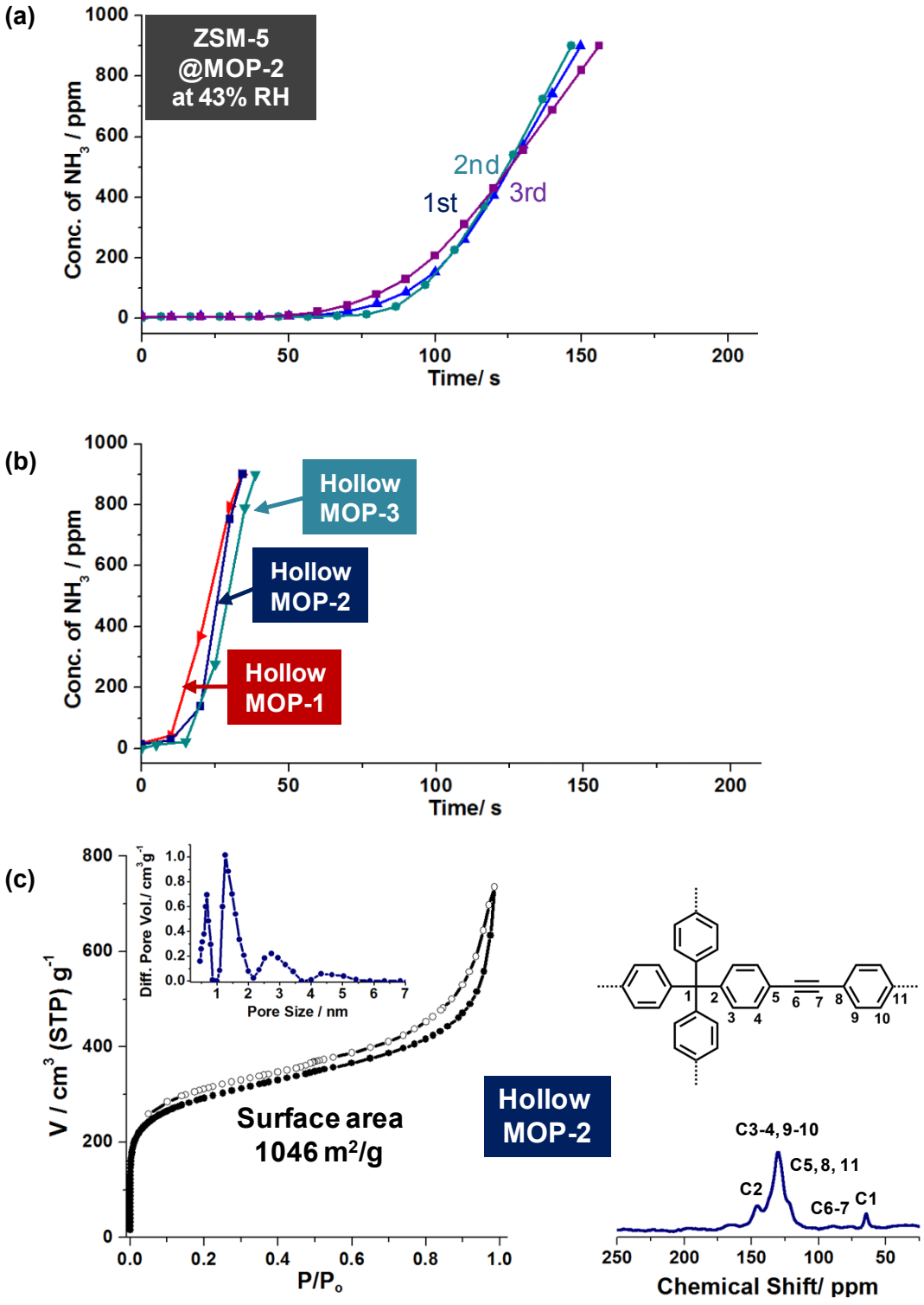

Fig. S5 NH_3 adsorption behavior of ZSM-5 (50 mg and 300 mg scale) under 43% RH and dry conditions.

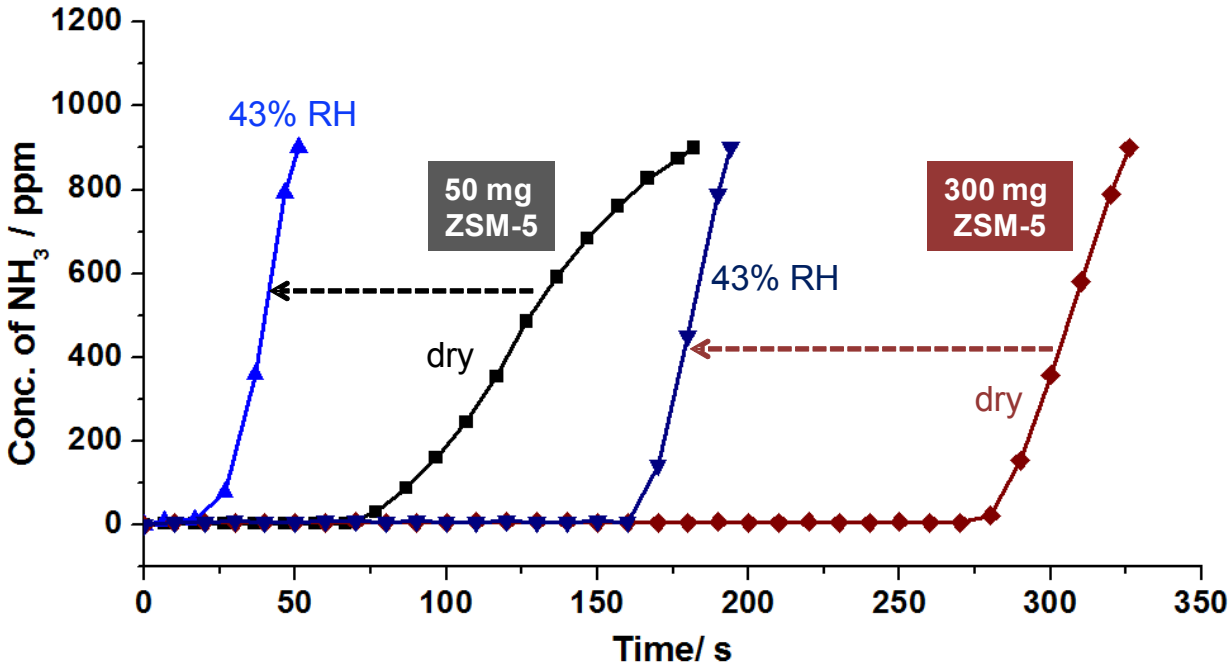

Fig. S6 Water sorption isotherm curves at 298K of ZSM-5 and ZSM-5@MOP-2 obtained by the standard volumetric procedure on a BELSORP-max instrument (BEL-Japan, INC). Pressure equilibrium points were collected automatically when the pressure change is within 0.5% in 500 s.