Supplementary Information for

Hollow Mesoporous Zeolite Microspheres: Hierarchical Macro-/meso-/microporous Structure and Exceptionally Enhanced Adsorption Properties

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Experimental Details

Synthesis of Materials: The fabrication process of HMZS involves three key steps: self-assembly under the directing by bi-templates of F127 and TPAOH, followed by post steam-assisted crystallization (SAC) for mesoporous zeolite structure (MZS) which has been published elsewhere [1,2] and mild alkaline etching (MAE) for hollow architecture. Its procedure is described in detail as follows. Firstly, 1.26 g F127 was added to 19.8 g distilled water under continuous stirring to get a clarifying solution. Then, 10.4 g tetraethylorthosilicate (TEOS, 99%) and 0.2 g aluminium isopropoxide [Al-(OPri)3, 99%] were added to the solution, subsequently. The resultant mixture was stirred vigorously until a homogenous mixture was obtained. After that, 4.06 g tetrapropylammonium hydroxide (TPAOH, 25%) was added dropwise into the sol. The molar ratio of the resultant sol was 0.5 Al2O3: 50 SiO2: 0.1 F127: 5 TPAOH: 1100 H2O. Stirring was continued to form a solidified gel and the whole stirring process was carried out at 36 ºC. The resultant wet gel was aged at 50 ºC for at least 12 h and subsequently, dried at 90 ºC for about 6 h until the mass of solid gel became unchanged. Then, this as-prepared gel was crystallized by the SAC method at 160 ºC for 10 h. The product was washed and filtrated repeatedly for several times and then dried at 100 ºC overnight. Finally, the product was calcined at 600 ºC for 10 h in air to remove the remained organic template and the obtained white powder was labelled as MZS. The HMZS was synthesized using MZS as precursors by MAE method. A typical procedure was described as follows: 0.5 g as-prepared MZS was added into 25 mL aqueous Na2CO3 solution (0.5M) with vigorously stirring. The mild alkaline treatment was kept at 60 ºC for 3 h. The resulting product was filtered, washed with distilled water and then dried at 100 ºC. The resultant white product was labelled as HMZS. The yield of HMZS, with the value of ca. 58%, in alkaline treatment was calculated by the mass ratio of samples before and after MAE procedure at 60 ºC for 3 h. The conventional ZSM-5 was bought from Shanghai Novel Chemical Co., Ltd. without further treatment and the alkaline treatment procedure of such ZSM-5 sample showed in Fig. S4 was the same as that for hollow mesoporous zeolites.

Adsorption of Mb: Methylene blue (MB) was used as model organic pollutants to test the dye adsorption properties of HMZS, MZS and ZSM-5. For that, aqueous solutions containing different concentrations of MB were prepared. 0.02 g of the as-obtained materials was added into 20 mL MB solution, and then the mixed solution was dispersed homogeneously by ultrasonication for 1 minute. The mixture solution was kept for adsorption equilibrium for as long as 3 hours, then the solid and liquid were separated and UV-Vis spectrophotometer was used to determine the remaining concentration of the MB in the solution. The adsorption isotherm of MB was obtained by the intensity of the UV-Vis absorption curves at $\lambda = 662$ nm. The adsorption dynamic tests were performed using MB solution with 150mg L^{-1}. At certain time intervals, 0.3 mL of the solution was taken out by centrifugation and then dilution to test the MB concentration by virtue of UV–Vis absorption technique.

Characterization: Powder XRD patterns were recorded on a Rigaku D/Max 2200PC diffractometer using Cu K_α radiation (40 kV and 40 mA) with the scanning rate 4 °min^{-1}. The N_2 sorption measurements were performed using Micromeritics ASAP 2020 porosimeters at 77 K. The mesoporous specific surface area, pore volume and the pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The micropore specific surface area and volume were calculated by the *t*-plot method. FTIR spectra were obtained in the range of 400–4000 cm^{-1} using a Nicolet iS10 with a resolution of 4 cm^{-1}. FE-SEM analysis was performed on JEOL JSM6700F and Hitachi S4800 electron microscopes. TEM images were obtained on a JEOL-2010F electron microscope operated at 200 kV. UV-Vis measurements were determined by a Shimadzu UV-3101PC spectrophotometer. The Al contents analysis of various catalysts were performed by ICP-AES with a Varian Vista AX ICP-AES spectrometer.

Figures and Tables

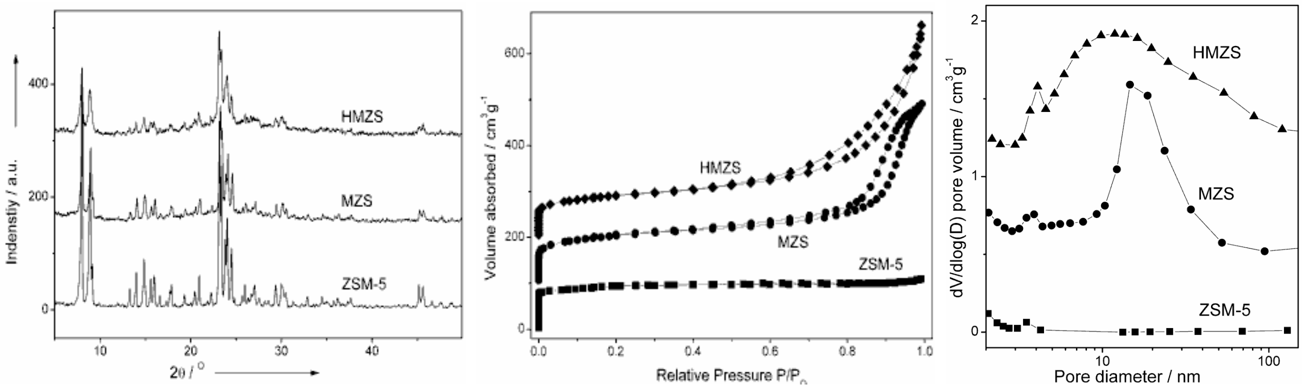

Figure S1. XRD patterns, N_2 sorption isotherms and pore size distributions of MZS (●), HMZS (▲) and conventional ZSM-5 zeolite (■). Isotherms of MZS and HMZS are offset by 100 and 200 cm^{3}g^{-1}, respectively.

Table S1. Chemical and textural properties of MZS, HMZS and ZSM-5.

Sample	Mole ratio of Si/Al[a]	S_{BET}[b] / m^{2}g^{-1}	S_{micro}[c] / m^{2}g^{-1}	$S_{external}$[c] / m^{2}g^{-1}	V_{micro}[c] / cm^{3}g^{-1}	V_{BJH}[d] / cm^{3}g^{-1}
MZS	68	465	190	275	0.08	0.59
HMZS	63	341	138	203	0.06	0.69
ZSM-5	66	322	216	106	0.10	0.17

[a] Determined by ICP-OES; Calculated by [b] BET, [c] t-plot and [d] BJH methods, respectively.

XRD patterns and N_2 sorption isotherms of the as-synthesized MZS, HMZS and ZSM-5 are shown in Figure S1. Both XRD patterns of MZS and HMZS clearly demonstrate the characteristic reflections of ZSM-5 indicating the favorable crystallinity. The sorption curve of MZS exhibits the typical type-IV isotherm with a H1 hysteresis loop and the capillary condensation occurs at high relative pressure indicating the large mesopore size, as further confirmed by the pore distribution. Comparatively, the sorption curve of HMZS exhibits H3 hysteresis loop indicating a broad pore distribution. The BET surface area of the sample decreased whereas the pore volume increased after alkaline treatment (Table S1), due to the destroy or broadening of mesopores, which is in good agreement with the reports of alkaline treatment.[3-5] Moreover, the creation of large voids in the interior of the spheres is not responsible for the pore volume increase calculated by BET method due to their too large size to induce capillary condensation of nitrogen gas.

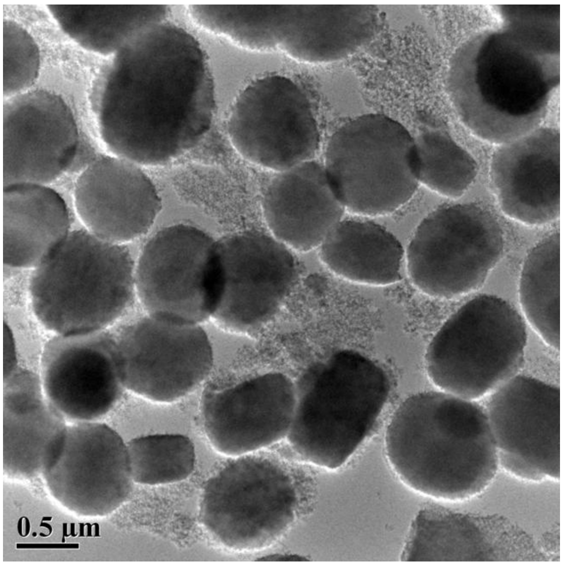

Figure S2. TEM images of MZS.

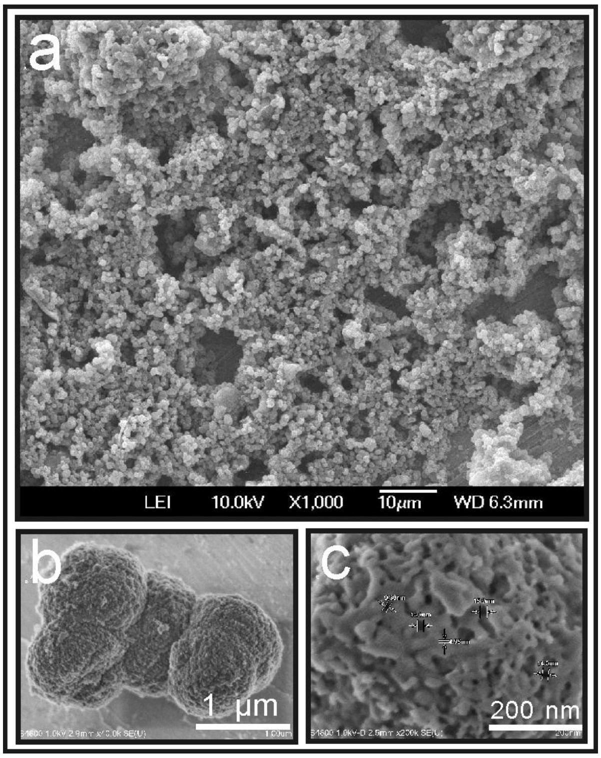

Figure S3. SEM images of HMZS: (a) a large amount of particles at lower magnification; (b) several aggregated particles; (c) a high resolution image of the particle surface in (b). The scales in (c) from left to right are 9.36, 13.9, 4.96, 15.9, 14.0 nm, indicating the broadened pore size distribution by alkaline etching corresponding to Figure S1.

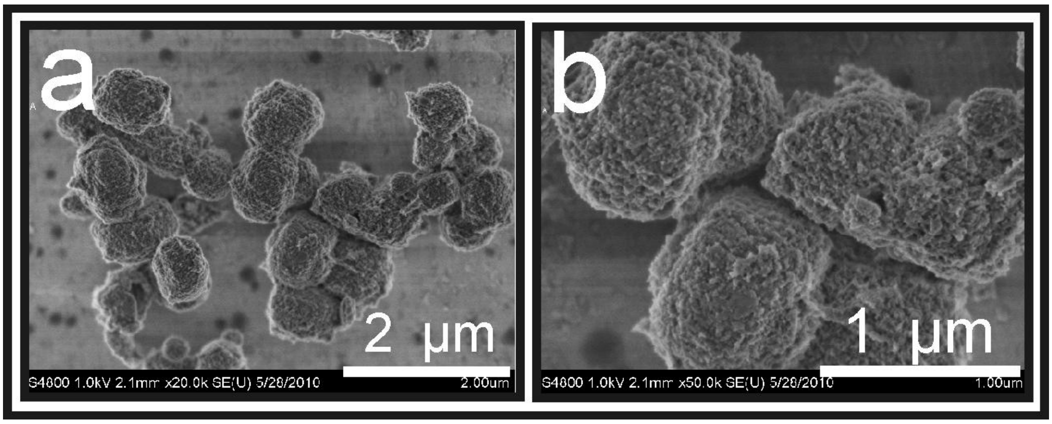

Figure S4. SEM images of HMZS after ultrasonic treatment showing the intact near-spherical morphology of the sample.

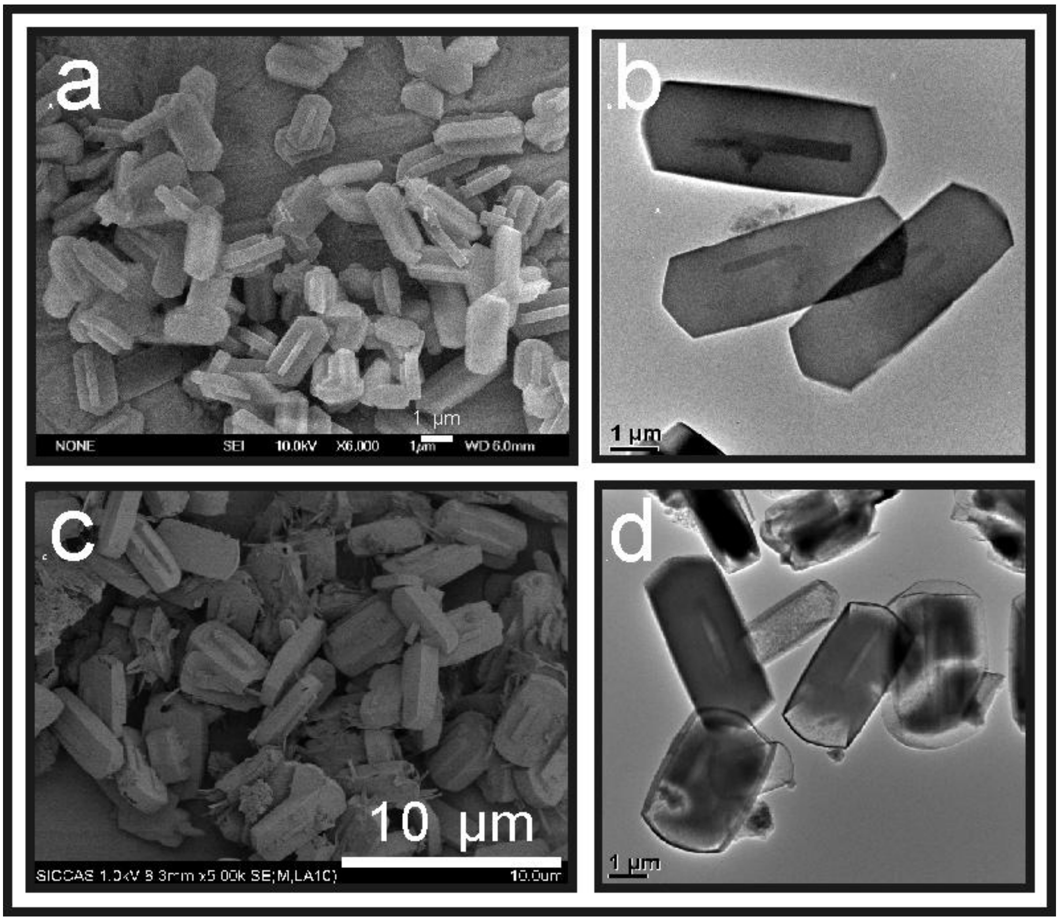

Figure S5. SEM and TEM images of conventional ZSM-5 before (a, b) and after (c, d) alkaline treatment for the same time period as that used for HMZS.

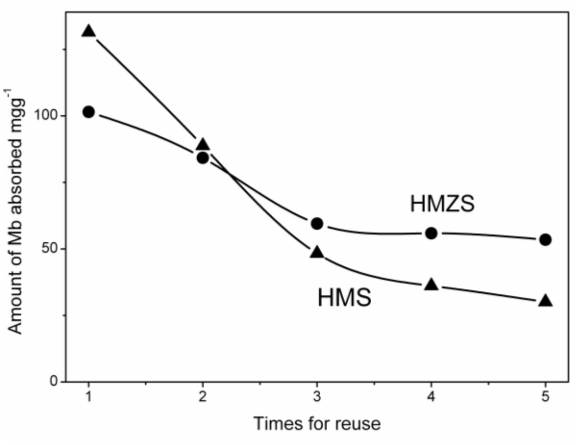

Figure S6. More interestingly, HMZS (●) and amorphous hollow mesoporous spheres (HMS, ▲), which were also synthesized using MAE method, are reused in the MB adsorption testing for 5 times.

References:

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