

Supporting Information

Synthesis of HKUST-1 and zeolite beta composites for deep desulfurization of model gasoline

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S1. Materials and Instrumentation

All solvents and reagents were purchased commercially without further purification. Powder X-ray diffraction (PXRD) data were collected with the laboratory Rigaku D/Max-2500 diffractometer with CuK α radiation in the 2θ range of $2\sim 50^\circ$ at a scanning rate of $2^\circ/\text{min}$. The Fourier transform infrared (FT-IR) spectra were recorded on a MAGNA FTIR-560 ESP spectrometer with KBr pellets in the range of $400\text{--}4000\text{ cm}^{-1}$. Thermogravimetric analyses (TGA) were performed on a METTLER TOLEDO TG/DSC 1 thermogravimetric analyser from Seiko under Ar (300ml/min) gas stream at a heating rate of $5^\circ\text{C}/\text{min}$ from room temperature to 800°C . The Fourier transform infrared (FT-IR) spectra were carried out on a MAGNA FTIR-560 ESP spectrometer with KBr pellets in the range of $400\text{--}4000\text{ cm}^{-1}$. The morphologies of the samples were obtained on a SU8010 SEM with an accelerating voltage of 10 kV. The nitrogen adsorption and desorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 static volumetric gas adsorption instrument. Prior to the sorption analysis, samples (0.1~0.2 g) in the analysis chamber were subject to a vacuum of 10-5 Torr at 150°C for 12 h. The specific surface area (SBET) was determined from the linear part of the BET equation ($P/P_0 = 0.05\text{--}0.3$).

S2. MOF Synthesis

HKUST-1 was synthesized as described by Schlichte et al.¹ 0.875 g $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$ (3.6 mmol) was dissolved in 12 mL de-ionized water and mixed with 0.42 g (2.0 mmol) of trimesic acid dissolved in 12 mL ethanol. The mixing solution was stirred for 30 min and then poured into 50 mL Teflon liner, placed in an autoclave, heated to 120°C for 12 h.

S3. Zeolite Beta Synthesis

3.1 nanocrystalline zeolite Beta

0.375 g silica sol (freeze dried prior to its use), 0.0062 g NaOH and 0.5mL deionized water were mixed with 0.82835 g of tetraethylammonium hydroxide (TEAOH, 20% aqueous solution) and stirred at 30-40 °C until clear. 0.0513 g aluminium isopropoxide(AIP) was dissolved in 0.82835 g of tetraethylammonium hydroxide (TEAOH, 20% aqueous solution) at 30-40 °C until clear. The alumina solution and 0.5 mL polystyrene beads were then added to the silica solution in turn under intensive stirring and the resultant clear mixture was transferred to an autoclave. The mixture was heated at 170 °C for 24 h. After the synthesis, the resin-zeolite beta composites were separated from the zeolite crystallized in the bulk, treated with 10-20mL 0.1 M ammonia solution in an ultrasonic bath for 5 min, rinsed several times by suspension in deionized water, decanted and dried at 60 °C. Finally, the organic macrotemplate was removed by combustion at 600 °C for 60 min after heating to this temperature with a heating rate of 1 °C /min.

3.2 zeolite beta microspheres

As described in previous literature,² 1.5 g silica sol (freeze dried prior to its use) and 0.0248 g NaOH were mixed with 3.3134 g of tetraethylammonium hydroxide (TEAOH, 20% aqueous solution) and stirred at 30-40 °C until clear. 0.2053 g aluminium isopropoxide(AIP) was dissolved in 3.3134 g of tetraethylammonium hydroxide (TEAOH, 20% aqueous solution) at 30-40 °C until clear. The alumina solution and 0.7816 g styrene divinylbenzene anion exchange resin beads were then added to the silica solution in turn under intensive stirring and the resultant clear mixture was transferred to an autoclave. The mixture was heated at 170 °C for 24 h. After the synthesis, the resin-zeolite beta composites were separated from the zeolite crystallized in the bulk, treated with 10-20 mL 0.1 M ammonia solution in an ultrasonic bath for 5 min, rinsed several times by suspension in deionized water, decanted and dried at 60 °C. Finally, the organic macrotemplate was removed by combustion at 600 °C for 60 min after heating to this temperature at a heating rate of 1 °C /min.

S4. HKUST-1/ Beta composites Synthesis

4.1 HKUST-1@nanosized zeolite beta composites

A typical synthetic procedure for HKUST-1 crystals is as follows: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.438 g, 1.5mmol) was dissolved in 12 mL of deionized water and mixed with 1,3,5 benzenetricarboxylic acid (BTC) (0.21 g, 1mmol) dissolved in 12mL of ethanol. The mixture was heated at 120 °C for 24 h in a 50 mL Teflon-lined steel autoclave. After cooling, 0.2 g of P123 was added and stirred for 2 h. Then 0.2 g of zeolite beta was added and stirred for an additional 2 h. The mixture was heated at 120 °C for 12 h in a 50 mL Teflon-lined steel autoclave. The obtained blue powder was filtered off, washed several times with distilled water and ethanol, and then dried at 120 °C overnight.

4.2 Preparations of zeolite beta microsphere@HKUST-1 composites

(1) Seed Deposition

The zeolite beta microspheres were dipped, in sequence, in (a) a 10mM $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ ethanol solution for 20 min, (b) ethanol for 5 min, (c) a 10mM H_3BTC ethanol solution for 40 min, and (d) ethanol for 5 min. The process from step (a) to step (d) was considered as a cycle. After cycling 5 times, the composites were dried at 60 °C for 30 min. This process is shown schematically in Scheme 1. The Cu^{2+} ions were exchanged into the surface and channels of beta zeolite, the portion of the carboxyl groups on H_3BTC bonded with Cu^{2+} and enabled the growth to continue. After the deposition of each layer, residual coordination sites still existed for the next deposition, and thus the seeding process could continue.

(2) Hydrothermal synthesis of zeolite beta microsphere@HKUST-1 composites

The seeded zeolite beta was crystallized for the synthesis of zeolite beta microsphere@HKUST-1 composites. 0.656 g $\text{Cu}_3(\text{BTC})_2 \cdot 3\text{H}_2\text{O}$ and 0.315 g H_3BTC were dissolved into 24 mL ethanol and water solution with v:v=1:1, and stirred for 30 min. The above-mentioned homogeneous solution was transferred to a Teflon-lined steel and then the seeded zeolite beta were added, after that the mixture was heated at 120 °C for 12 h in an autoclave. The pellets were filtered and washed several times by deionized water and ethanol. Finally, the pellets were dried at 100 °C for 5 h.

S5. Adsorption Test

The model fuels were prepared by dissolving a desired amount of thiophene in isooctane, and the sulfur content ranges from 0 to 400 ppmw (parts per million by weight). In a typical experiment, adsorbents (20 mg) were mixed with a model fuel (2 mL). Then the mixture was sonicated for 5 min, after that it was stood undisturbedly for a certain time. The sulfur or nitrogen content of the treated model fuels was determined by a RPP-2000SN sulfur nitrogen analyzer. Before desulfurization, Zeolite beta were calcined at 550 °C for 5 h, HKUST-1 and composites were degassed in vacuum at 150 °C for 2 h. The sulfur adsorption capacity (q_e , mmol S g^{-1}) was calculated according to Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{mM} \times 10^{-3} \quad (1)$$

where C_0 and C_e are the sulfur concentrations with the unit of mg S L^{-1} in the model oil before and after desulfurization respectively, V is the volume of the model oil in milliliter, m is the gram mass of adsorbents, and M is the molar mass of sulfur (32 g mol^{-1}).

S6. Morphology

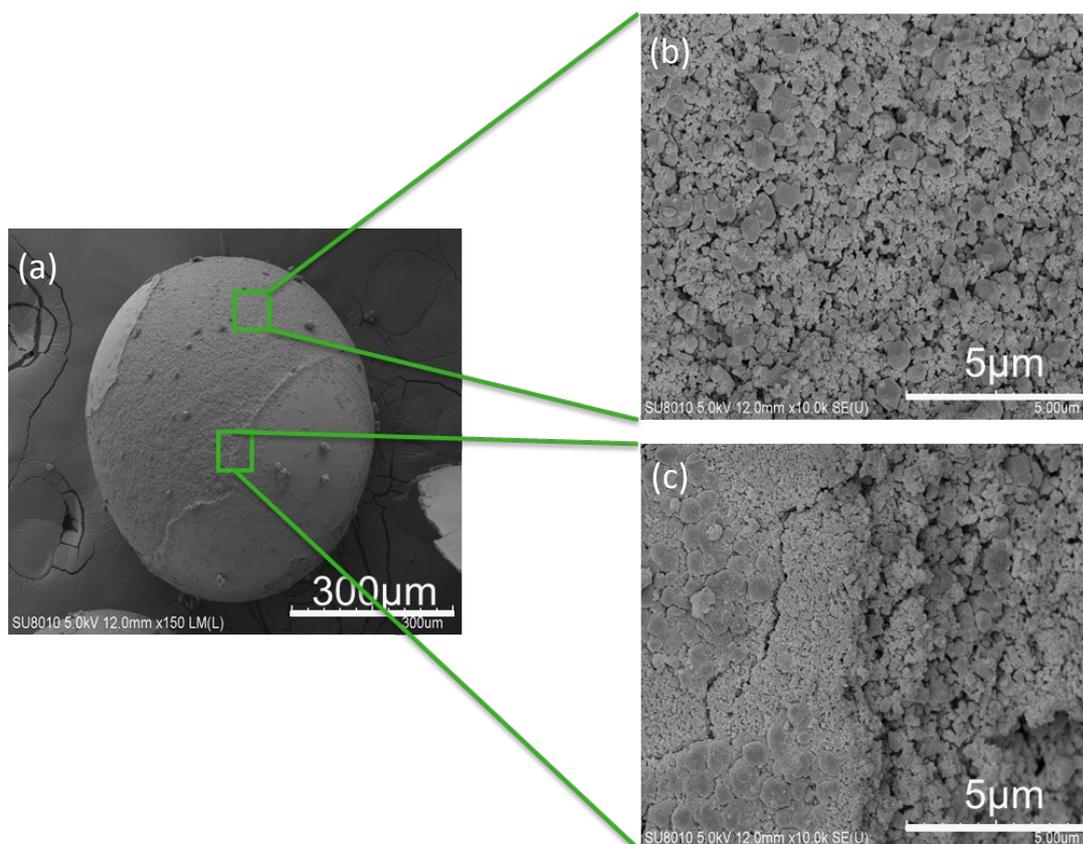


Figure S1 SEM images of (a) zeolite beta microspheres@HKUST-1 and (b,c) the magnified region of green border on the surface of zeolite beta microspheres@HKUST-1 composite.

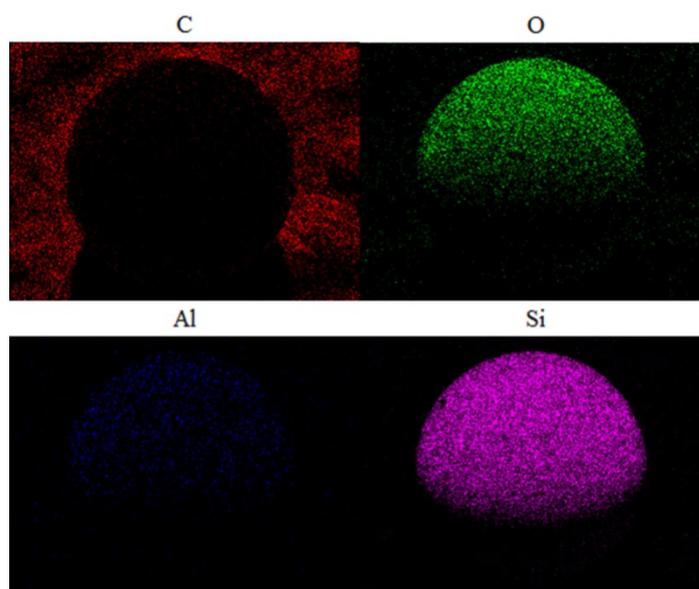


Figure S2. EDX mapping of C, O, Al, Si of HKMB

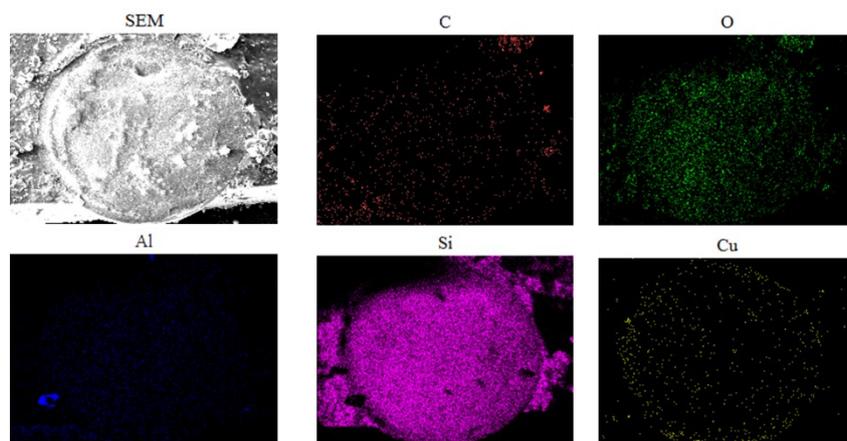


Figure S3. Cross-section EDX mapping of C, O, Al, Si, Cu of HKMB

S7. Color change

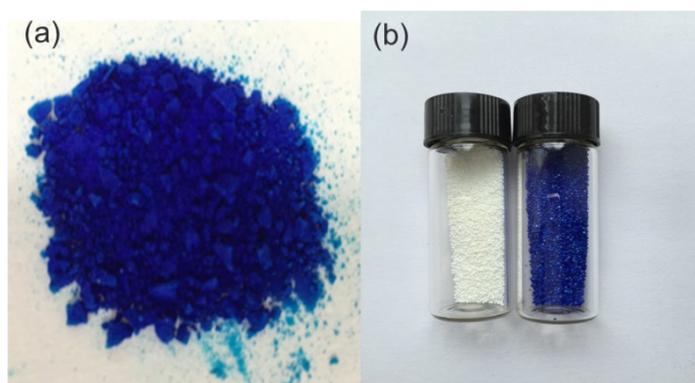


Figure S4. Optical photographs of (a) HKUST-1 and (b) MB (left) and HKMB (right).

S11. References

- (1) Schlichte, K.; Kratzke, T.; Kaskel, S. *Microporous and Mesoporous Materials*. **2004**, *73*, 81-88.
- (2) Tosheva, L.; Mihailova, B.; Valtchev, V.; Sterte, J. *Microporous and mesoporous materials*. **2001**, *48*, 31-37.