

Hydrothermally stable macro-meso-microporous materials:

Synthesis and application in heavy oil cracking

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Supplementary materials

2. Experimental

2.1 Materials

Triblock copolymer P123 (EO₂₀PO₇₀EO₂₀, Mw=5800) was purchased from Sigma-Aldrich Co. LLC. Water glass (containing 28.3 % SiO₂ and 8.8 % Na₂O), sodium hydroxide (NaOH), sulfuric acid (H₂SO₄) and aluminium sulfate (Al(SO₄)₃·18H₂O) were obtained from Tianjin Guangfu company. Sodium Dodecyl Sulfate (SDS) was purchased from Beijing Beihua Fine Chemicals Co. (China). Styrene and Sodium Persulfate Na₂S₂O₈ were obtained from Guangdong Xilong Chemical Co. (China).

2.2 Synthesis procedure

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2.2.1 Preparation of zeolite Y precursors:

Y precursors was prepared according to literature ⁹.

2.2.2 Preparation of PS microspheres:

PS microspheres were obtained according to literature ¹⁹.

2.2.3 Synthesis of hierarchical materials

PS microspheres obtained in step 2.2.2 and P123 were dissolved in deionized water to obtain the dual templates. Zeolite Y precursor solution obtained in step 2.2.1 is added to the dual templates, and pH of the resulting gels are adjusted to 2.0 by dropwise adding 5.0 mol/L H₂SO₄ solution. The resulting gel mixture was stirred at 40 °C for 20 h and then transferred into an autoclave to crystallize at 110 °C for 24 h. Crystallization products are collected by filtration, drying and calcination for obtaining the MSA sample. MSA was hydrothermally treated at 100 % vapor, 800 °C for 2 h, and denoted as A-MSA.

2.2.4 Catalytic cracking performance tests

USY zeolite was obtained from Lanzhou Petrochemical Company. Cat-1 was prepared from Kaolin (65%), Alumina gel (10%), and USY (25%), Cat-2 was prepared from Kaolin (60%), Alumina gel (10%), MSA (5%) and USY (25%). DO-75 was the commercial catalyst obtained from Lanzhou Petrochemical Company. The three catalysts were crushed, sieved to 20-40 mesh, and steamed at 800 °C, 100% water vapor for 2 h before using.

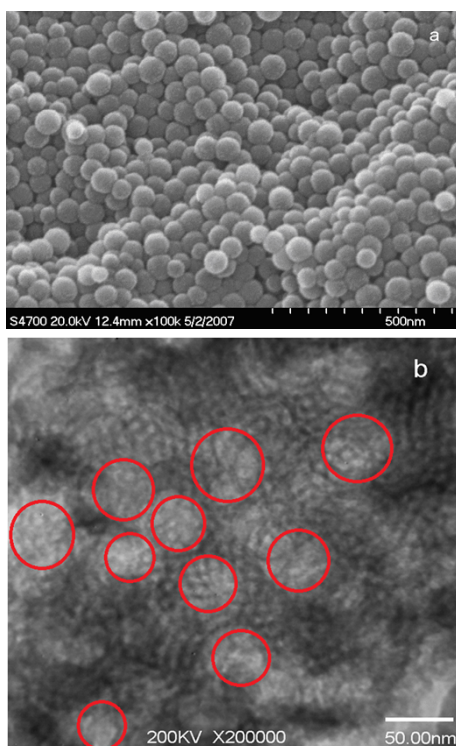
Heavy oil catalytic cracking tests were carried out in a micro-activity testing (MAT) unit by the pulse method according to the literature ¹¹.

2.3 Characterizations

Powder X-ray diffraction (XRD) was carried out with a Miniflex X-ray automatic diffractometer (Rigaku, Japan) using Cu K α ($\lambda = 0.154056$ nm) radiation at room temperature and operated at 30 kV and 50 mA. The powder diffractograms of the samples were recorded over a range of 2θ values from 0.5° to 8° . The scanning rate was set at $1.00^\circ/\text{min}$. The values of unit cell parameter were calculated using the formula $a = 2d_{100}/3^{1/2}$, where d_{100} represents the d-spacing value of the (100) diffraction peak in the XRD patterns. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were carried out with a Hitachi S-4700 electron microscope (Hitachi, Japan) at 200 kV and a Rigaku H-800 electron microscope (JEOL, Japan) at 20 kV, respectively. The specimens for TEM observation were prepared by epoxy-resin-embedded microsectioning and mounting on a copper grid. N₂ adsorption and desorption isotherms were measured on an ASAP 2405 N instrument (Micromeritics, Germany) at liquid nitrogen temperature. The Brunauer-Emmett-Teller (BET) method was used to calculate the surface areas of the samples (S_{BET}). The surface areas (S_{Mic}) and volumes (V_{Mic}) of micropores were calculated by using the V-t plot method. The sizes of mesopores were derived from Barrett-Joyner-Halenda (BJH) models. The Fourier transform infrared (FT-IR)

absorption spectra in the zeolite framework vibration region were obtained with IR Prestige-21 spectrometer (Shimadzu, Japan). Powder samples were dispersed in KBr pellets for FT-IR analysis. The spectrum was acquired in a wavenumber range between 400 and 1500 cm^{-1} at 2 cm^{-1} resolution. ^{27}Al solid-state NMR experiments were performed on a Varian Unity Inova 300 spectrometer (Varian, USA) equipped with a double resonance 6 mm ChemagneticsTM MAS probe and operated with frequency at 78.17 MHz, pulse width at 1.6 μs , radiofrequency field strength at 50 G, pulse delay at 1 s, spinning rate at 5 kHz.

Supplementary Figures



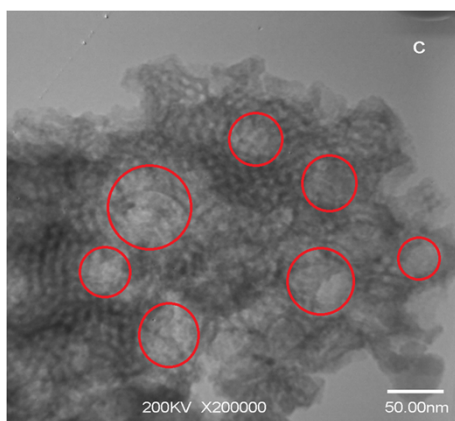


Fig. S1 (a) SEM image of PS microspheres; (b)TEM of MSA; and (c) TEM of A-MSA. The macropores were marked by the red lines.

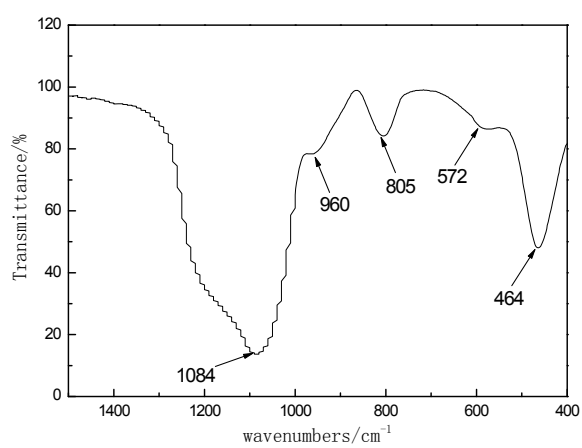


Fig. S2 FT-IR spectra of MSA

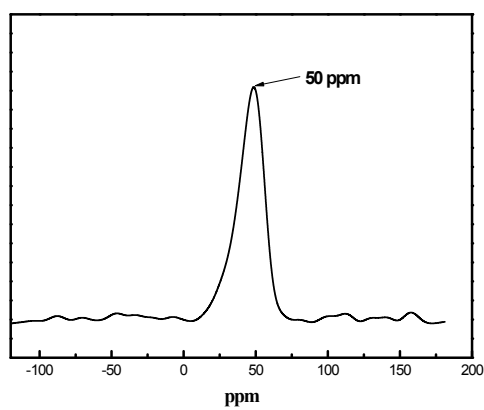


Fig. S3 Solid-state ²⁷Al-NMR spectrum of MSA.