Facile one-pot solvent-free synthesis of hierarchical ZSM-5 for methanol to gasoline conversion

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Supporting information:

Materials:

$Na_2SiO_3.9H_2O$ (99%, Shanghai Runjie Chemical Reagent Company), Fumed silca (Aladdin Chemical Regent Company), Tetrapropylammonium bromide (TPABr, 98%, Aladdin Chemical Regent Company), Tetraethylammonium bromide (TEABr, 98%, Adamas Chemical Regent Company), Tetrabutylammonium bromide (TBABr, 98%, Adamas Chemical Regent Company), NH_4Cl (99%, Shanghai Runjie Chemical Reagent Company), $NaAlO_2$(99%, Shanghai Runjie Chemical Reagent Company), activated carbon (Macklin Chemical Regent Company), methanol (99%, Shanghai Runjie Chemical Reagent Company), DDI water was obtained from a Millipore system. All chemicals were analytical grade and were used as received without further purification.

Preparation of SH-ZSM-5

19.5 g of $Na_2SiO_3 \cdot 9H_2O$, 5.2 g of fumed silica, 3.6 g of TPABr, 1.76 g of activated carbon and 6.3 g of NH_4Cl with different amount of $NaAlO_2$ (0.1~1.2 g) were mixed together one by one. After grinding for 20 s in a mechanical grinder, the mixture was transformed to an autoclave and heated at 180 ^oC for 24~48 h. After filtration at room temperature, drying at 100 ^oC and calcination at 550 ^oC, a series of

crystallized products of SH-ZSM-5 with different Si/Al ratio were obtained.

Characterization

The morphology of SH-ZSM-5 was examined by a scanning electron microscope (SEM, Hitachi, S4800). TEM, HTEM and selected-area electron diffraction patterns were measured by JEM-2100F, JEOL Ltd., Japan. X-ray diffraction (XRD) patterns were obtained using a X-ray diffractometer (Rigku, ultima IV, 40 kV, 40mA) with Cu Kα (λ=1.5406 A) radiation. Thermal degradation measurements were performed on a Thermogravimetric analysis (TGA) (NETZSCH, STA 449F3). MAS NMR spectra were recorded on a Varian Infinity plus 400 spectrometer. The reference materials of NMR for the chemical shift (in ppm) were kaolinite for ^{29}Si, $Al(H_2O)_6^{3+}$ for ^{27}Al. BET surface areas and pore size were measured by N_2 adsorption-desorption isotherms (Micromeritics, physisorption analyzer, ASAP 2020). NH_3-TPD measurement were carried out on a TP5080 (Xianquan, Tianjin), the catalysts (0.2 g, 40~60 mesh) were pretreated at 500 °C in a N_2 flow for 60 min before the measurement, then by the adsorption of NH_3 at 100 °C for 30 min. After saturation, the catalyst was purged by N_2 flow for 30 min to remove the physically adsorbed NH_3 on the sample. And then, the desorption process of NH_3 was carried out from 100 to 600 °C with a heating rate of 10 °C/min.

Catalytic test: methanol to gasoline reaction (MTG)

MTG reaction was carried out with a fixed-bed tubular steel reactor with an inner diameter of 12 mm and a length of 550 mm at atmospheric pressure. 2.0 g of catalyst (20 ~ 40 mesh) was loaded in between two layers of quartz wool in each run. The sample was pretreated in flowing nitrogen at 400°C for 3 h and then cooled to 380 °C to carry out the reaction. Gaseous methanol was introduced into the reactor with the weight hourly space velocity (WHSV) of 1.0 h^{-1}. Products from the reactors were analyzed on-line by a GC-2014C gas chromatographs equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The vent gas

and cooled hydrocarbons from condenser were analyzed by FID-detector with HP-PLOR/Q capillary column, whereas CO_x in gas and methanol in cooled water were detected by TCD-detector with TDX-01 packed column.

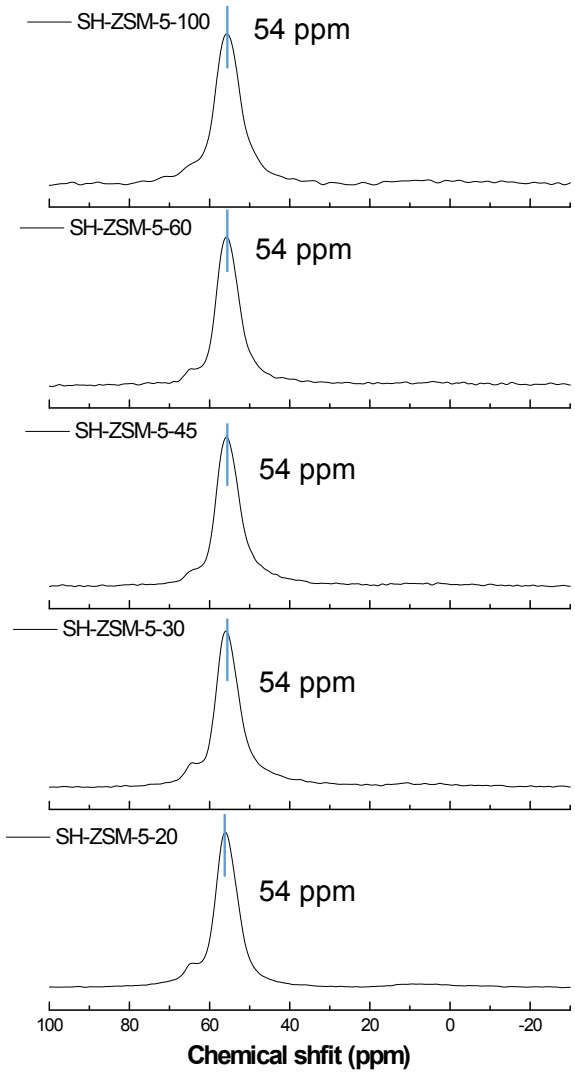


Fig. S1. ^{27}Al MAS NMR spectrum of SH-ZSM-5 with different Si/Al ratio.

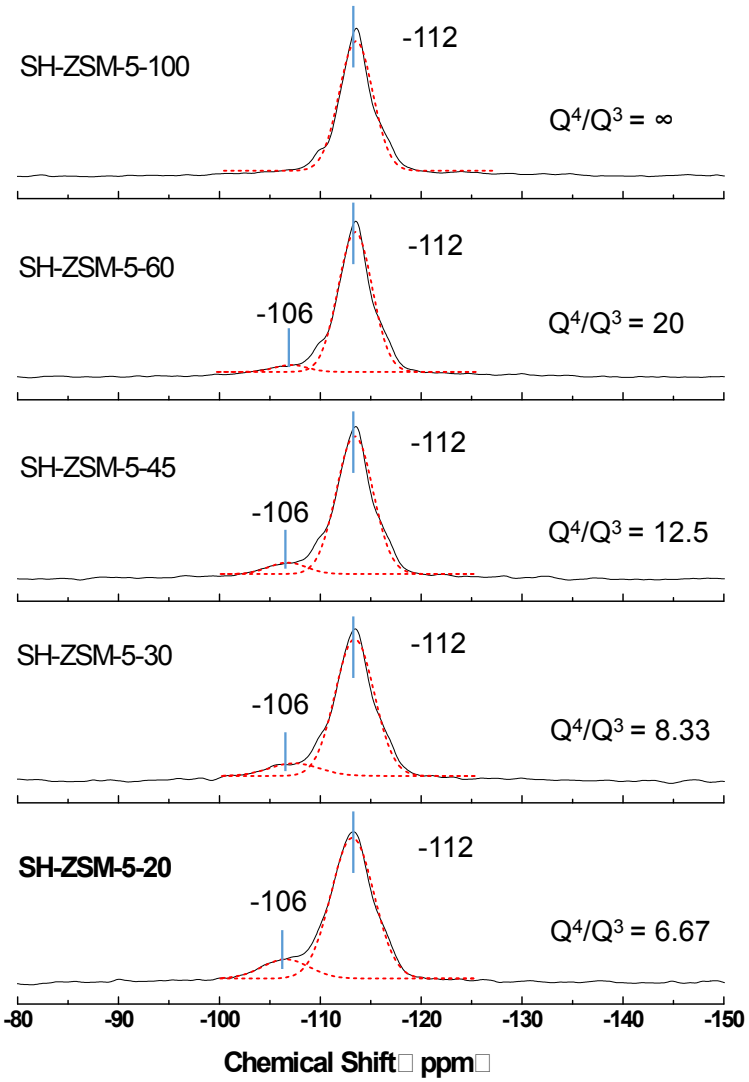


Fig. S2. ^{29}Si MAS NMR spectrum of SH-ZSM-5 with different Si/Al ratio.

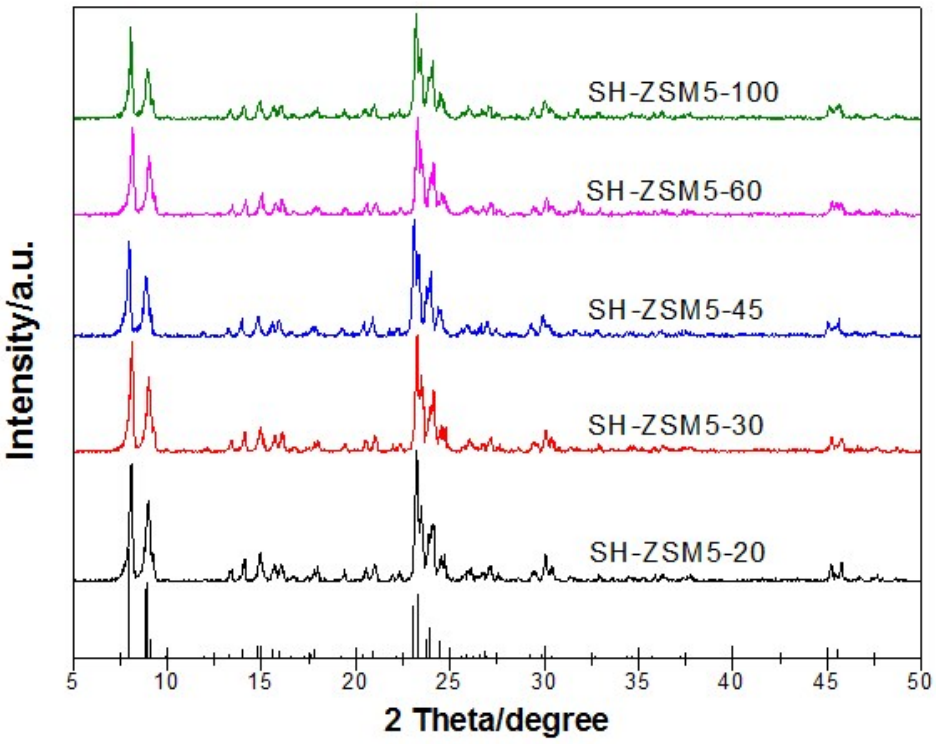


Fig. S3. XRD patterns of prepared SH-ZSM-5 with different Si/Al ratio.

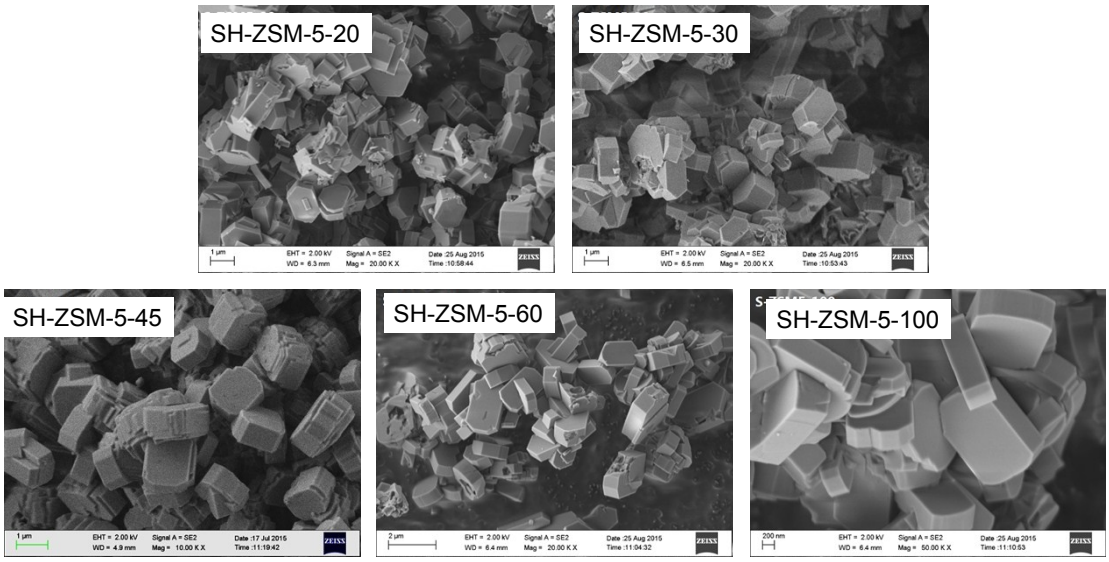
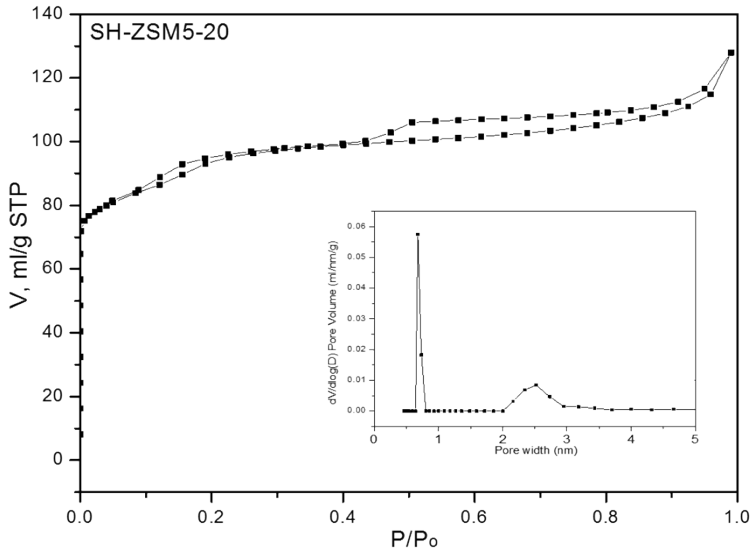
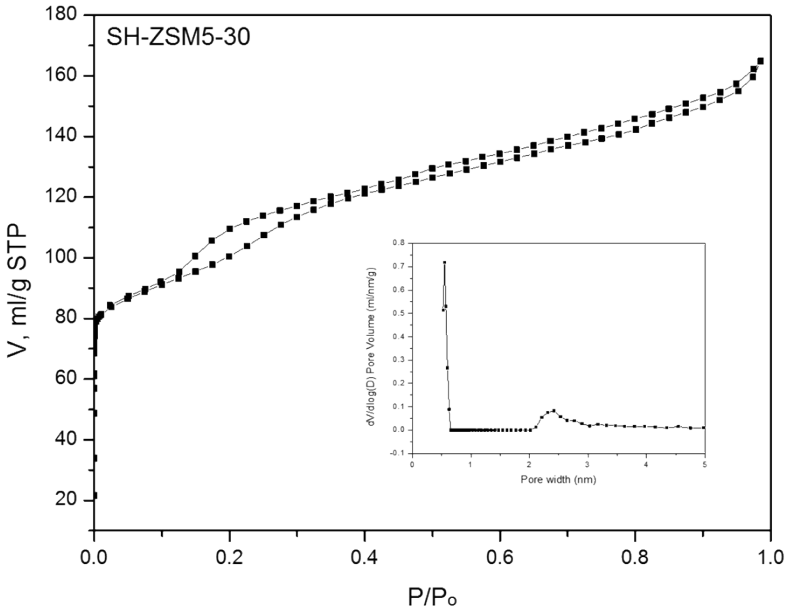
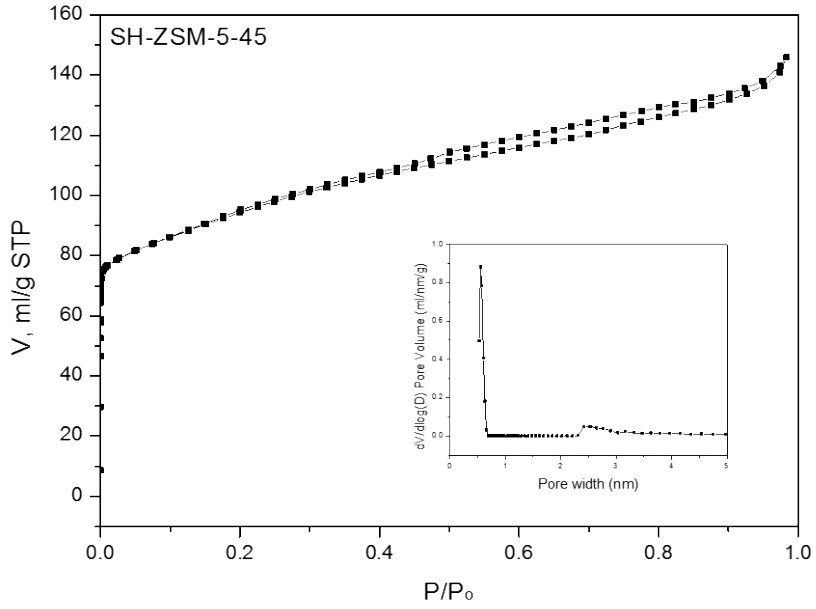
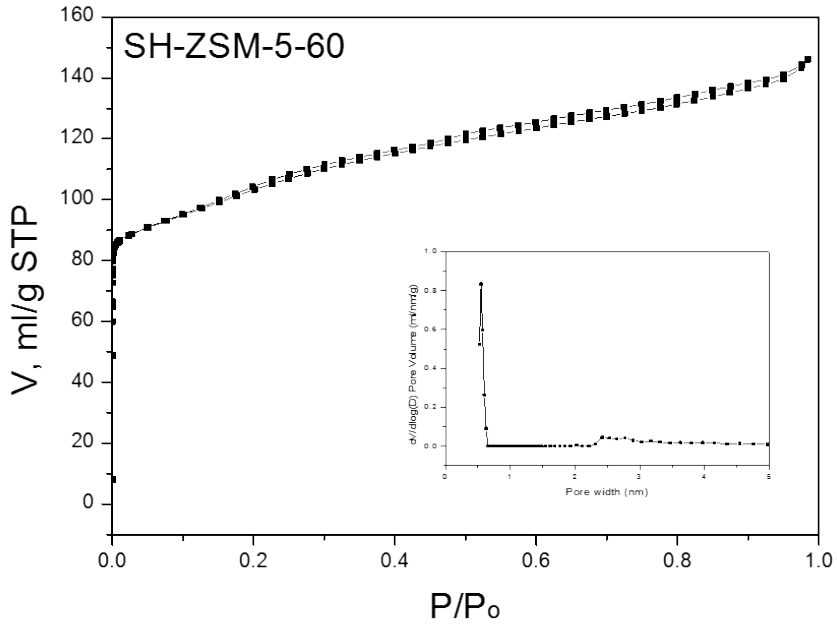


Fig. S4. SEM images of prepared SH-ZSM-5 with different Si/Al ratio.


SH-ZSM5-20
V, ml/g STP
P/Po
dV/dlog(D) Pore Volume (ml/nm/g)
Pore width (nm)


SH-ZSM5-30
V, ml/g STP
P/Po
dV/dlog(D) Pore Volume (ml/nm/g)
Pore width (nm)


SH-ZSM-5-45
V, ml/g STP
P/Po
dV/dlog(D) Pore Volume (ml/nm/g)
Pore width (nm)


SH-ZSM-5-60
V, ml/g STP
P/Po
dV/dlog(D) Pore Volume (ml/nm/g)
Pore width (nm)

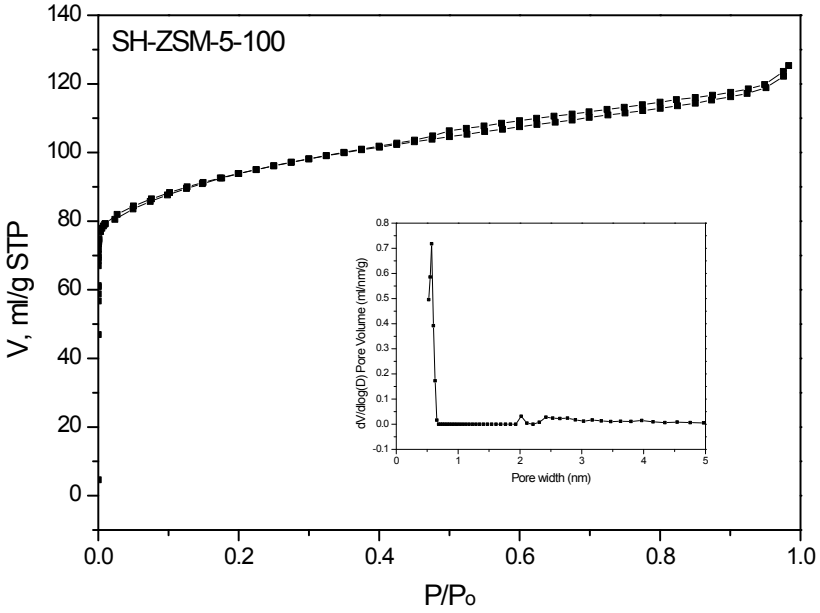


Fig. S5. N_2 adsorption-desorption isotherms and PSD of SH-ZSM-5 zeolites with different Si/Al ratio.

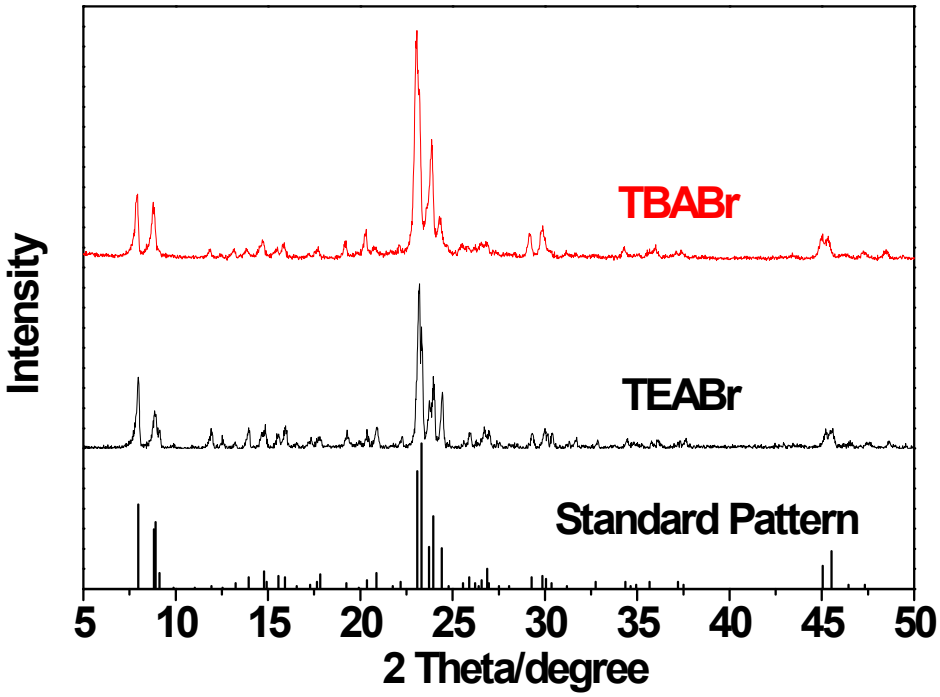


Fig.S6 XRD patterns of prepared materials using TEABr and TBABr

The detail information of activated carbon used in this work:

Activated carbon is provided from Macklin Chemical Regent Company, and chemical compositions of AC are: Carbon (>99.5%), Heavy metals (Pb<0.01 ppm, Fe<0.01 ppm, Zn<0.1 ppm), Sulfur compounds (<0.15%). Fig.S6 describes the morphology of AC. It is shown that the particles of activated carbon are aggregated from the SEM images.

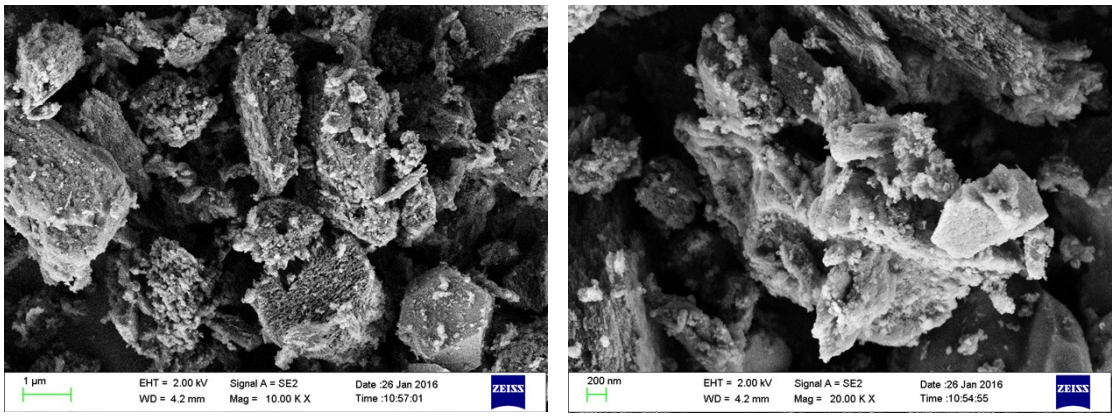


Fig. S7. SEM images of activated carbon

Table S1. Textural properties of the prepared hierarchical SH-ZSM-5 samples

Samples	Si/Al	$S_{BET}(m^2/g)$	$S_{micro}(m^2/g)$	$S_{Ext}(m^2/g)$	$V_{sum}(cm^3/g)$	$V_{micro}(cm^3/g)$
SH-ZSM-5-20	21.6	299	213	85.8	0.20	0.12
SH-ZSM-5-30	31.9	357	261	96.0	0.16	0.13
SH-ZSM-5-45	44.7	377	302	74.6	0.16	0.14
SH-ZSM-5-60	62.5	337	253	83.7	0.15	0.12
SH-ZSM-5-100	109.3	349	295	54.1	0.14	0.13

Si/Al ratio was determined by XRF analysis.