Versatile Route to Zeolite Single Crystals with Controlled Mesoporosity: *in-situ* Sugar Decomposition for Templating of Hierarchical Zeolites

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Synthesis

Silica-carbon composite

The silica-carbon composite was prepared by the following procedure. The required amount of sucrose was dissolved in 5 g of water with heating. 5 g of mesoporous SiO_2 (Merck, silica gel 100, particle size 0.063-0.200 mm, pore diameter 15 nm, pore volume 1.0 ml/g) was impregnated with this solution to incipient wetness. The resulting material was dried overnight at room temperature and then calcined in a flow of Ar at 673 K for 15 hours.

Mesoporous Na-ZSM-5

The mesoporous Na-ZSM-5 material was prepared according to the following procedure. In a 100 ml flask, 33.83 g of 20% TPAOH, 8.50 g of H_2O, 0.53 g NaOH and 0.08 g of $NaAlO_2$ was added with stirring until a clear solution was obtained. After that, the silica-carbon composite obtained above was added to the mixture and left for 1 hour. The composition of the resulting synthesis gel was 1 Al_2O_3 : 181 SiO_2 : 36 TPA_2O : 15 Na_2O : 1029 H_2O. The carbon containing zeolite synthesis gel was introduced into a stainless steel autoclave, heated to 453 K and kept there for 72 h. Then, the autoclave was cooled to room temperature, the product was suspended in water, filtered by suction, resuspended in water, and filtered again. Finally, the product was dried at 383 K for 10 h, and the organic template and the carbon was removed by controlled combustion in air in a muffle furnace at 823 K for 20 h.

Mesoporous Na-ZSM-11.

The mesoporous Na-ZSM-11 material was prepared according to the following procedure: In a 100 ml flask, 21.58 g of 40% TBAOH, 30 g of H_2O, 0.53g NaOH and

0.08 g of $NaAlO_2$ was added with stirring until a clear solution was obtained. After that SiO_2 with partially decomposed carbohydrate was added to the mixture, which was left for 1 hour with stirring. The composition of the resulting synthesis gel was 1 Al_2O_3 : 181 SiO_2 : 36 TBA_2O : 15 Na_2O : 1029 H_2O. Then the gel was introduced into a stainless steel autoclave, heated to 180 °C and kept there for 72 h. Then, the autoclave was cooled to room temperature, the product was suspended in water, filtered by suction, resuspended in water, and filtered again. Finally, the product was dried at 110 °C for 10 h and the organic template and the partially decomposed carbohydrates were removed by controlled combustion in air in a muffle furnace at 550 °C for 20 h.

Characterization

X-ray powder diffraction (XRPD) patterns were recorded using Cu -Kα radiation in the 2θ interval 5-50° using a Philips PW1820 powder diffractometer. The samples were studied after the zeolite synthesis and combustion of the carbon material.

Nitrogen adsorption and desorption measurements were performed at liquid nitrogen temperature on a Micromeritics ASAP 2020. The samples were outgassed in vacuum at 473 K prior to measurements.

Hg porosimetry was conducted with a Quantachrome mercury intrusion equipment.

Scanning electron microscopy (SEM) was performed on a Philips XL20 FEG. The calcined zeolite samples were placed on a carbon film and Pt was evaporated onto the sample for approximately 20 minutes to achieve sufficient conductivity. About 20 images were recorded for each sample.

Transmission electron microscopy (TEM) images were obtained with a JEM 2000FX employing an accelerating voltage of 300 kV. The samples were suspended in ethanol and dispersed on a copper grid coated with holey carbon film. 15 images were obtained from each sample.

Table S1.

Sample	$\frac{n(sucrose)}{n(SiO_2)}$	V_{micro} $(cm^3/g)^a$	V_{meso} $(cm^3/g)^b$	BET area $(m^2/g)^c$
ZSM-5	0	0.14	0.0	374
ZSM-11	0	0.13	0.0	365
ZSM-11	0.58	0.14	0.04	372
ZSM-5	0.58	0.14	0.04	359
ZSM-5	0.87	0.14	0.05	361
ZSM-5	1.75	0.15	0.08	356

[a] Calculated by *t*-plot method.[b] Calculated by BJH method.[c] Calculated by BET method.

Figure S1. XRPD pattern of mesoporous ZSM-5 prepared with C/Si=1.75.

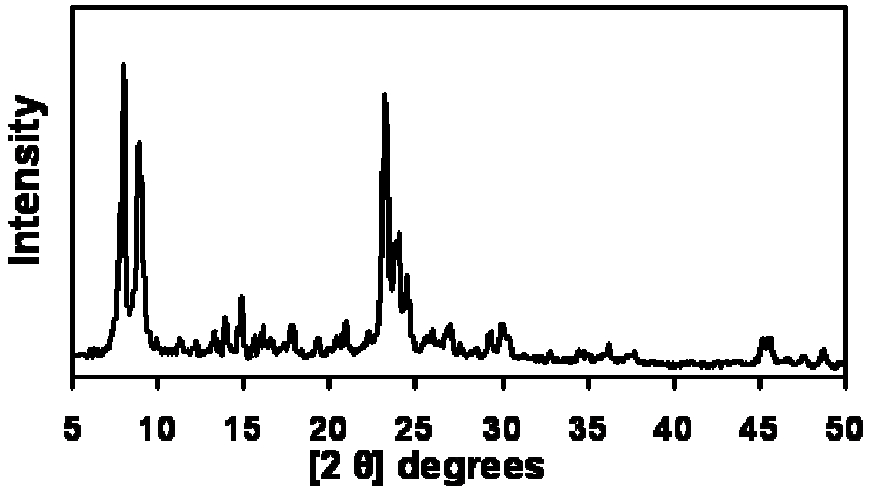

Figure S2. XRPD pattern of mesoporous ZSM-11 prepared with C/Si= 0.58.

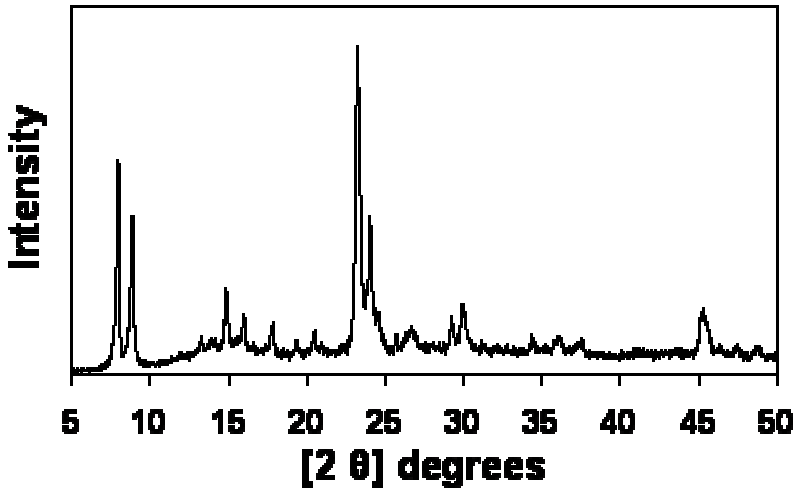

Figure S3. Nitrogen adsorption/desorption isotherms for ZSM-5 zeolites prepared with different amounts of sugar used to prepare the silica/carbon composite. The isotherms are shifted vertically to allow comparison of the individual samples