

Electronic Supplementary Information

Crystal-like Microporous Hybrid Solid Nanocast from Cr-MIL-101

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Experimental section

Materials. The following materials, 3-aminopropyltriethoxysilane (98%, Aldrich), resorcinol (Riedel-de Haen) and paraformaldehyde (95%, Aldrich) were used as received without further purification.

Synthesis of Cr-MIL-101 (denoted B). MIL-101 was synthesized from $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and terephthalic acid in a hydrothermal reaction according to the literature.¹³ The crude product was activated in a microwave oven using 15 mL of DMF at 150 °C for 30 min and twice using 15 mL ethanol at 150 °C for 30 min. After each activation step Cr-MIL-101 was centrifuged and dispersed in the corresponding solvent (or dried at 75 °C after the last step). This sample has the BET surface area and the total pore volume of $3116 \text{ m}^2 \text{ g}^{-1}$ and $1.78 \text{ cm}^3 \text{ g}^{-1}$, respectively.

Synthesis of Si-Cr-MIL-101 (denoted A). Cr-MIL-101 was dispersed in THF and 3-aminopropyltriethoxysilane was added. The dispersion was stirred for 12 h at room temperature. Afterwards it was washed three times using ethanol, centrifuged and dispersed in fresh ethanol. This sample has the BET surface area and the total pore volume of $1712 \text{ m}^2 \text{ g}^{-1}$ and $1.05 \text{ cm}^3 \text{ g}^{-1}$, respectively.

Synthesis of A-C-x. A-C-x was synthesized using the incipient wetness impregnation technique. In a typical procedure, 300 mg of A pretreated under dynamic vacuum (1 mbar) at 150 °C overnight was impregnated with an ethanolic solution of resorcinol (0.30 mL, containing 76.3 mg of resorcinol) with vigorous agitation under an argon atmosphere. The mixture was kept in the sealed Schlenk tube for 2 h at room temperature. 41.6 mg of paraformaldehyde in a small vial was added to the Schlenk tube, followed by evacuation

for 1 h to remove the ethanol. The polymerization was carried out by heating the tube at 55 °C for 24 h and then at 95 °C for 48 h. The obtained PRF/Si-MIL-101 composite (denoted A-P-x) was carbonized at 650 °C for 3 h at a heating rate of 1 °C/min in a tube furnace under a flow of argon. After cooling to room temperature, black powders were obtained. These were kept in argon for several hours. This step is essential and needs to be performed carefully. When air was slowly introduced into the tube oven, the top of the black powders turned grey whereas the bottom part remained black.

To completely fill the pores of A, the maximum amount of resorcinol was calculated based on its density and the pore volume of A. The influence of resorcinol loadings (20, 50, and 80 vol% of the maximum amount of resorcinol) on the final structures was investigated. To ensure a uniform impregnation, the calculated amount of resorcinol was dissolved in defined amounts of ethanol equal to the pore volume of A. The materials were denoted as A-P-x and A-C-x, respectively, where A, P and C indicate the Si-MIL-101 template, RF polymer and carbonized product, respectively and x corresponds to the volume ratio (%) of resorcinol to A.

For comparison, unfunctionalized Cr-MIL-101 was also tested as template for the preparation of nanocast carbons. Similar to the Si-Cr-MIL-101 series (A-series), the obtained samples are named as B-P-x and B-C-x, where B indicates the Cr-MIL-101 template, x represents the volume ratio (%) of resorcinol to MIL-101, P and C have the same meaning as above.

Characterization. X-ray diffraction (XRD) patterns were recorded on a Stoe STADIP diffractometer in the Bragg-Brentano (reflection) geometry. Nitrogen sorption

isotherms were measured on an ASAP2010 analyzer at 77K. Before the measurements, the samples were degassed at 200 °C for at least 6 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}) using adsorption data in a relative pressure range from 0.06 to 0.2. The total volumes were estimated from the adsorbed amount at a relative pressure P/P_0 of 0.9. The NLDT pore size distribution is calculated from the adsorption branch with a mixture pore model of cylinder, sphere and split shapes. TEM images were obtained with a HF2000 electron microscope from Hitachi equipped with a cold field emission gun. The acceleration voltage was 200 kV. Samples were prepared dry on a lacey carbon grid. High resolution scanning electron microscopy (HR-SEM) and scanning transmission electron microscopy (STEM) images of the samples were taken using a Hitachi S-5500 ultrahigh resolution cold field emission scanning electron microscope operated at 30 kV.

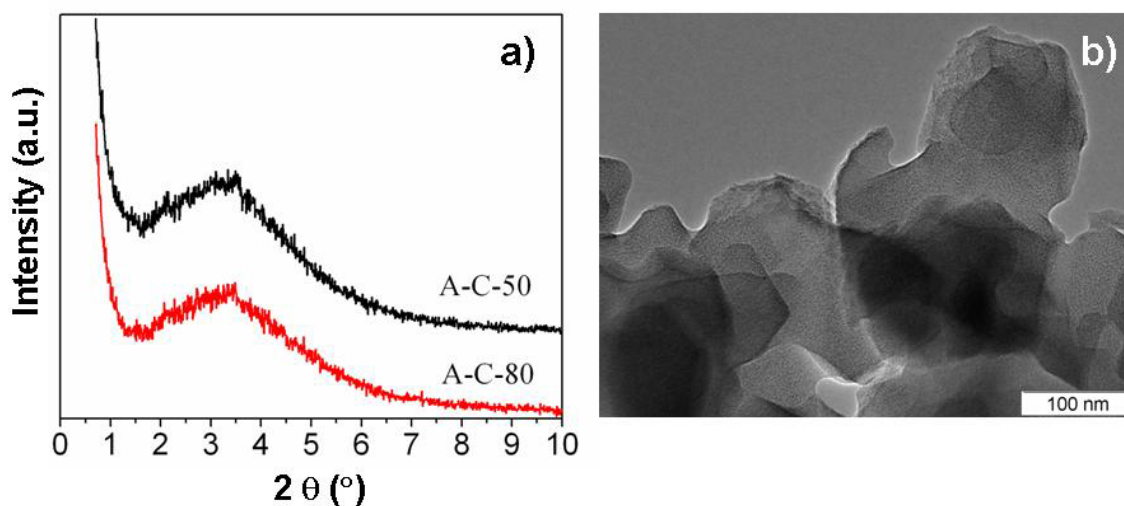


Fig. S1 (a) Low-angle XRD patterns of A-C-50 and A-C-80, (b) TEM image of A-C-80.

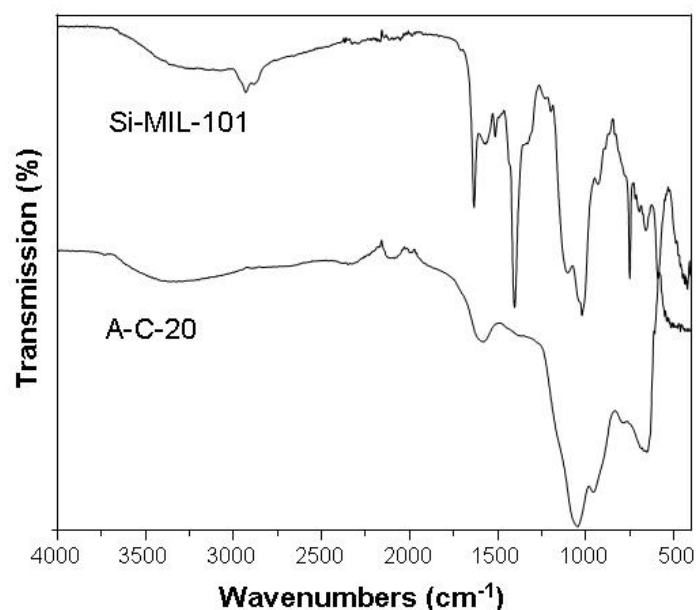


Fig. S2 FT-IR spectra of the crystal-like microporous hybrid solid A-C-20 and aminopropyl triethoxysilane functionalized Si-MIL-101(aliphatic $\text{-CH}_2\text{-}$ asymmetric (2930 cm^{-1}) and symmetric (2865 cm^{-1}) stretch, carboxylate asymmetric stretch (1628 cm^{-1}), aromatic $\text{C}=\text{C}$ stretch (1559 and 1507 cm^{-1}), rocking Si-O-CH_3 (1194 cm^{-1}), Si-O-C asymmetric stretch (1093 cm^{-1}) and rocking Si-CH_2 (741 cm^{-1})).

Table S1 EDX Analysis of A-C-20.

C	O	Si	Cr
32.91	17.70	20.41	28.98
31.62	22.13	18.51	27.74
17.82	26.16	23.33	32.69
33.66	20.65	18.53	27.16