

Amidoxime-Functionalized Nanocrystalline Cellulose-Mesoporous Silica Composites for Carbon Dioxide Sorption at Ambient and Elevated Temperatures

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Materials

Microcrystalline cellulose (MCC) (Avicel® PH-102, degree of polymerization (DP) ~ 100-300), was obtained from FMC BioPolymer (Newark, DE). 3-isocyanatopropyltriethoxysilane (ICPTS) was purchased from Alfa Aesar, Johnson Matthey Company, Ward Hill, Massachusetts. 3-hydroxyglutaronitrile (HGN) was purchased from TCI America, Portland, Oregon. Diisopropylethylamine (DEA) and hydroxylamine hydrochloride (NH₂OH.HCl) were purchased from Sigma Aldrich. Pluronic P123 (EO₂₀PO₇₀EO₂₀) triblock copolymer was donated by BASF Corporation, Florham Park, New Jersey. 36 % HCl, NaOH and 95 % ethanol were purchased from Fisher Scientific, Pittsburgh, Pennsylvania. Tetraethylorthosilicate (TEOS) was purchased from Gelest Inc., Morrisville, Pennsylvania. Deionized water (DW) was obtained from in-house Ion pure Plus 150 Service Deionization ion-exchange purification system and AquaOne (Amarillo, TX). All reagents were of analytical grade and were used without further purification.

Characterization

The methods used for characterization of the samples studied were analogous as those presented in [1-3]. Namely, nitrogen adsorption was measured at -196°C using ASAP 2010 volumetric analyzer (Micromeritics, Inc., Norcross, GA). All samples were out gassed under vacuum at 110°C for 2 h prior to adsorption measurements.

Thermogravimetric (TG) profiles were recorded in flowing nitrogen using high resolution thermogravimetric TGA Q-500 analyzer (TA Instruments, Inc., New Castle, DE), from 25 to 720°C in flowing nitrogen with a heating rate of 10°C / min using a high resolution mode. The initial weight of each sample analyzed ranged 5-15 mg. TG profiles were used to obtain

information about the extent of the template removal, cyanopropyl functionalization, and amidoximation.

Bruker Avance (III) 400WB NMR spectrometer (Bruker Biospin Corporation, Billerica, MA, USA) with MAS triple resonance probe head using zirconia rotors 4 mm in diameter^{1,2,41} was used to record ¹H-¹³C cross polarization (CP) MAS NMR spectra. H-¹³C CP-MAS NMR spectra were acquired at 100.63 MHz for ¹³C and 400.13 MHz for ¹H. In each measurement, the MAS rate was 5 KHz, ¹H $\pi/2$ pulse length was 3.5 μ s and pulse delay was 2.0 s. TPPM20 ¹H decoupling sequence was used during acquisition. The ¹³C chemical shifts were referenced 66.6 ppm of p-dioxane. ¹H-²⁹Si cross polarization (CP) MAS NMR spectra were recorded at 79.49 MHz for ²⁹Si and 400.13 MHz (¹H) at MAS rate 5 KHz. ¹H $\pi/2$ pulse length was 4.5 μ s and pulse delay 3.0 s. Two-pulse phase modulated TPPM15 decoupling sequence was used during acquisition. The ²⁹Si chemical shifts were referenced to TMS (0 ppm).

Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G2 F20 microscope. Prior to TEM analysis, the sample powders were dispersed in ethanol by moderate sonication at concentrations of ~5-10 wt. %, followed by deposition of samples on a Lacy carbon coated, 200-mesh, copper TEM grid by dipping into the sample suspension and then dried under vacuum at 80°C for 20 h.

Room temperature CO₂ adsorption measurements

CO₂ adsorption measurements were carried out similarly as in [1-3] using an ASAP 2020 volumetric adsorption analyzer (Micromeritics, Inc., GA). These measurements were performed for selected cyanopropyl- and amidoxime-containing NCC-silica composites in the pressure range up to 1.2 atm at 25°C using ultrahigh purity (99.99 %) gaseous CO₂. Prior to adsorption analysis, each sample was outgassed under vacuum at 110°C for 2 h.

CO₂ chemisorption and TPD measurements

CO₂ chemisorption and TPD experiments were performed similarly as in [1-3] using a Micromeritics Auto Chem II Chemisorption Analyzer (Micromeritics, Inc., GA), equipped with a thermocouple detector (TCD). Approximately 20-100 mg of each sample was loaded in the quartz tube micro reactor supported by quartz wool and subjected to pretreatment at 320°C for 10 min before CO₂ adsorption using a heating rate of 10°C/min in flowing helium (at a rate of 50 cm³/min). Next, the sample was cooled to 120°C at a cooling rate of 10°C/min, exposed to pulse of 5 % CO₂-He (50 cm³/min) as a loop gas, kept for 3 min and allowed for return to baseline. Recording was taken every 0.1 seconds and repeated until peaks became equal. Finally, post CO₂ pulse purge was applied in flowing helium (50 cm³/min) for 30 min. In the TPD experiments, the samples were heated up to 320°C using a heating rate of 5°C/min and kept at this temperature for 90 min. The amounts of desorbed CO₂ were obtained by integration of the desorption profiles, with reference to the TCD signals calibrated for known volumes of analyzed gases.

Calculations

The measured nitrogen adsorption isotherms were analyzed similarly as in [1-3]. Namely, the Brunauer-Emmett-Teller specific surface areas (S_{BET}) were calculated from the N_2 adsorption isotherms in the relative pressure range of 0.05-0.2 using a cross sectional area of 0.162 nm^2 per nitrogen molecule. The single-point pore volume (V_{sp}) was estimated from the amount adsorbed at a relative pressure (p/p_0) of ~ 0.98 . The pore size distributions (PSD) were calculated using adsorption branches of nitrogen adsorption-desorption isotherms by the improved KJS method calibrated for cylindrical pores [4]. The volume of fine pores (micropores and small mesopores below 3 nm), V_{mic} , was calculated by integration of the PSD curve up to 3 nm. The pore width (W_{max}) was obtained at the maximum of the PSD curve.

References

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