

Mesoporous metal organic framework-boehmite and silica composites

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Synthesis

Synthesis of copper-containing HKUST-1 materials was performed as follows: 0.420g of 1, 3, 5-benzenetricarboxylic acid (H₃BTC, 98%, Acros Organics) were dissolved in 24ml of water-ethanol (50% V/V) followed by adding 0.882g of copper (II) nitrate trihydrate [Cu(NO₃)₂·3H₂O, Acros Organics] at room temperature. The sol formed was quickly transferred to Teflon lined microwave autoclaves. These were hydrothermally treated in microwave (CEM Mars 5) at 140°C for 30-120min using 300W. The same synthesis procedure was employed to synthesize MOF in the presence of triblock copolymer, polyethylene oxide-polypropylene oxide-polyethylene oxide of general formula (EO)₂₀-(PO)₇₀-(EO)₂₀, known as Pluronic P123, which in the amount of 0.65g was added to the reaction mixture. For the synthesis of MOF-boehmite composites, approximately 1.30g of Pluronic P123 were dissolved in 12ml of anhydrous ethanol, followed by the same amounts of H₃BTB and Cu(NO₃)₂·3H₂O used for the pure MOF-5 materials. The boehmite (AlOOH Catapal A, Sasol), 3.6, 7.2 and 14.4mmol, was quickly dispersed in 12ml of water and concentrated nitric acid (HNO₃), [H⁺]/[Al³⁺] = 0.10, and added to the Cu-H₃BTC-P123 sol. Each sol was transferred to the Teflon lined microwave autoclaves and hydrothermally treated at 40°C for 60min and then at 140°C for 120min. For the comparison, a silica-containing material was prepared. For the latter, the same amounts of copper nitrate and H₃BTC, and 0.98g of P123 were dissolved in 24ml of ethanol-water (50% V/V) followed by 3.6, 5.5 and 7.2mmol of tetraethoxysilane (TEOS, Acros Organics). These samples were hydrothermally treated in microwave for 1hr at 40°C and 120min at 140°C. All materials were filtered, thoroughly washed with ethanol and water and dried at 100°C overnight after hydrothermal synthesis.

MOF materials were labeled according to microwave synthesis time as MOF-*x*, where *x* = 30, 120 and 180min, similar the sample prepared with the addition of Pluronic P123 denoted as MOF-P-*x*. The composites containing SiO₂ or Al₂O₃ were labeled according to the formula: Si(*y*)-MOF and Al(*y*)-MOF, where *y* is the Si or Al/Cu molar ratio, since all samples were treated for 120min under microwave irradiation.

Characterization

Materials were characterized by thermogravimetric analysis (TG), nitrogen adsorption at -196°C, powder X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The TG measurements for as-synthesized materials were performed using a high resolution mode of the TA Instruments TGA 2950 thermogravimetric analyzer. The TG profiles were recorded up to 800°C in flowing air using a heating rate of 10°C min⁻¹.

Nitrogen adsorption isotherms were measured at -196°C using ASAP 2010 and 2020 volumetric adsorption analyzers manufactured by Micromeritics (Norcross, GA). Before adsorption measurements, all samples were degassed under vacuum for at least two hours at 200°C. The specific surface area of the samples was calculated using the BET method within the relative pressure range of 0.01 to 0.10. The micropore volumes were estimated on the bases of α -plot

analysis in the range of 0.8-1.25 of standard adsorption (α_s) for all composites samples and in the α_s range of 1.0-1.5 for pure MOF samples.

The X-ray diffraction patterns were recorded on a PANalytical. Inc. X'Pert Pro (MPD) Multi Purpose Diffractometer with Cu K α radiation (0.1540nm) using an operating voltage of 40kV and 40mA, 0.02° step size and 6s step. Microscope glass slides were used as sample holders for all measurements. The samples were manually ground prior to the XRD analysis and all measurements were performed at room temperature.

For scanning electron microscopy analysis (SEM), samples were manually ground using Agatha mortar, mounted on graphite tape and carbon coated in SPI Module carbon coater. All samples were imaged by a Hitachi S-4300 Field Emission SEM (FE-SEM) at an accelerating voltage of 2 to 15kV and 350 to 45000x magnification. The EDX spectra were collected using an Oxford INCAx-sight EDX and accelerating voltage of 10 to 15kV, with Cu calibration and 15mm working distance.

Table S1. Crystallographic parameters for all materials studied.

Sample	Phase identification	Unit cell parameter	FWHM* (°)
MOF-30	Cu ₃ (BTC) ₂ (H ₂ O) ₃	a=26.35 Å cubic	0.21
MOF-P-30	Cu ₃ (BTC) ₂ (H ₂ O) ₃	a=26.37 Å cubic	0.14
MOF-120	Cu ₃ (BTC) ₂ (H ₂ O) ₃	a=26.36 Å cubic	0.16
Al(1)-MOF-120	Cu ₃ (BTC) ₂ (H ₂ O) ₃	a=26.33 Å cubic	0.11
Al(2)-MOF-120	Cu ₃ (BTC) ₂ (H ₂ O) ₃	a=26.33 Å cubic	0.14
Al(4)-MOF-120	New phase	Monoclinic a = 11.68 Å b = 19.16 Å c = 9.60 Å β = 111.52°	
Si(1)-MOF-120	Cu ₃ (BTC) ₂ (H ₂ O) ₃	a=26.32 Å cubic	0.13
Si(1.5)-MOF-120	Cu ₃ (BTC) ₂ (H ₂ O) ₃ + [Cu ₂ (OH)(BTC)(H ₂ O)]*2H ₂ O	a=26.35 Å cubic**	0.11
Si(2)-MOF-120	Cu ₃ (BTC) ₂ (H ₂ O) ₃	a=26.37 Å cubic	0.11
Si(1.5)-MOF-60	Cu ₃ (BTC) ₂ (H ₂ O) ₃ + [Cu ₂ (OH)(BTC)(H ₂ O)]*2H ₂ O	a=26.33 Å cubic**	0.10
Si(1.5)-MOF-180	Cu ₃ (BTC) ₂ (H ₂ O) ₃	a=26.41 Å cubic	0.10

*FWHM- Full Width at Half Maximum calculated for the most intense peak of Cu₃(BTC)₂(H₂O)₃ phase.

**Unit cell parameter of Cu₃(BTC)₂(H₂O)₃ phase.

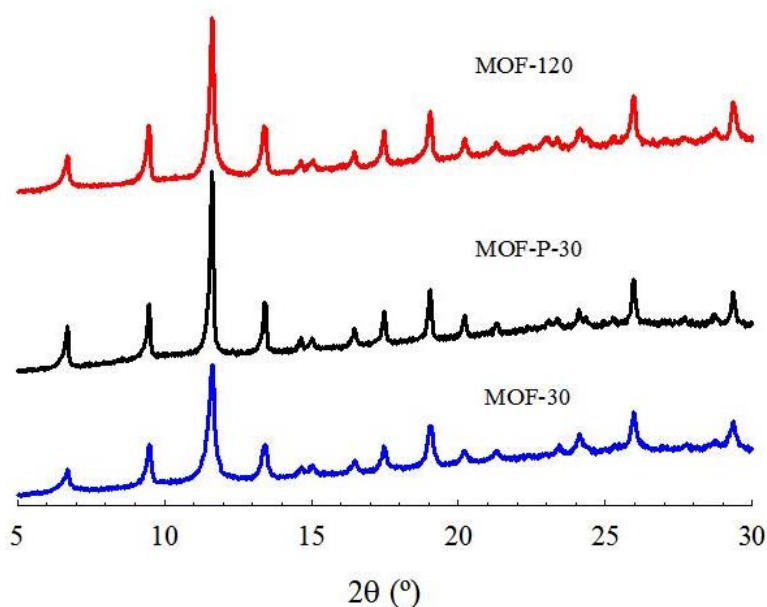


Figure S1. XRD patterns for pure MOF samples including the sample prepared with the addition of P123 (MOF-P-30).

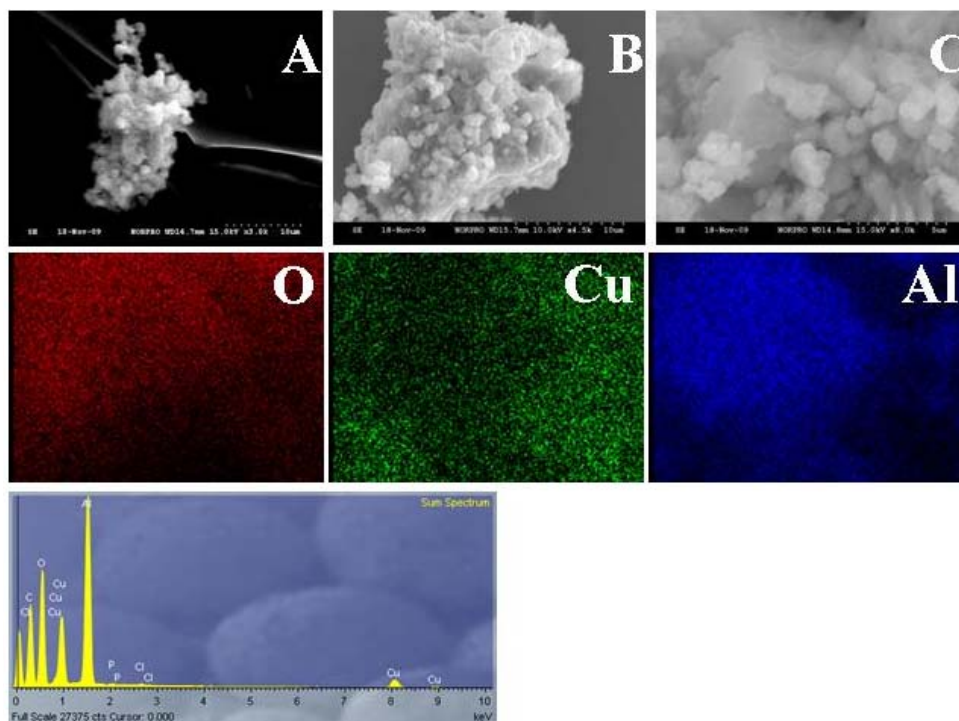


Figure S2. SEM images for two different particles of sample Al(2)-MOF (A) and (B); SEM image in (C) higher magnification of selected area on particle shown in (B) and its corresponding elemental mapping for O, Al and Cu and EDX data. Carbon tape and coating contributed to the EDX signal, whereas low intensity peaks for P and Cl result from impurities found in the commercial boehmite used for synthesis of Al(γ)-MOF.

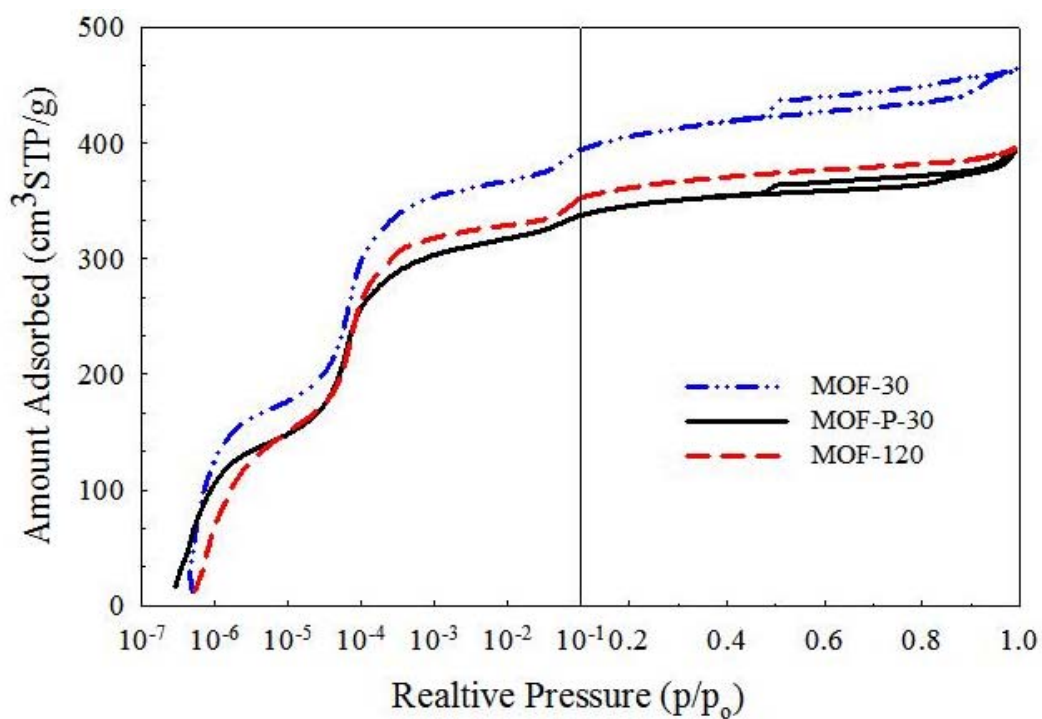


Figure S3. Nitrogen adsorption isotherms for the reference MOF samples.

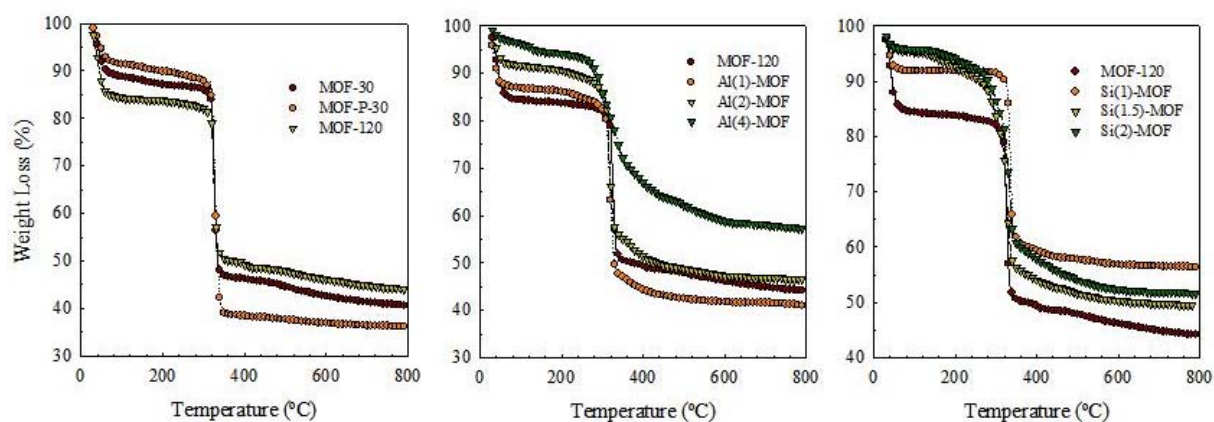


Figure S4. TGA decomposition profiles for all materials studied.

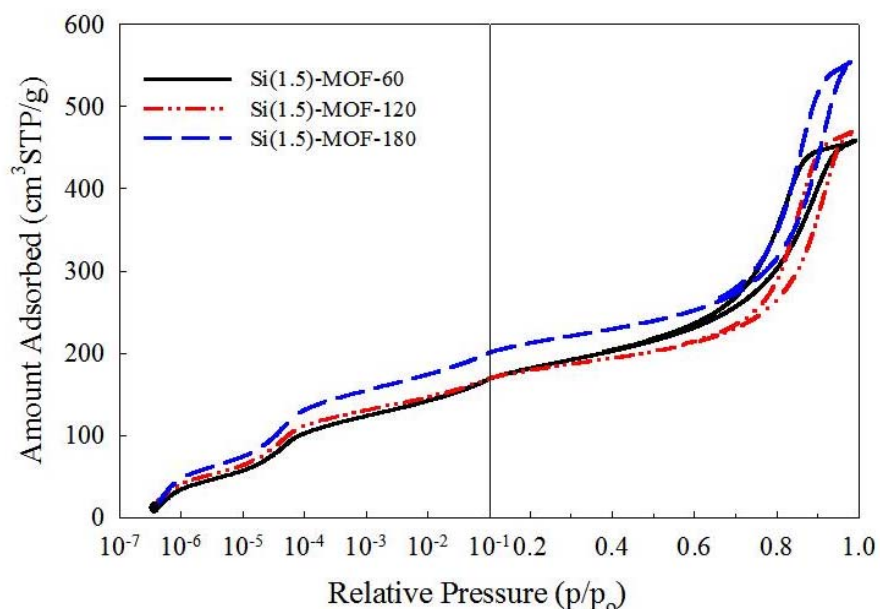


Figure S5. N₂ adsorption isotherms at -196°C for the MOF-silica composites synthesized with the same Si/Cu ratio and different times of microwave irradiation; as can be seen from the plots, both the total and micropore volumes can be improved by extending the microwave treatment up to 3hr.

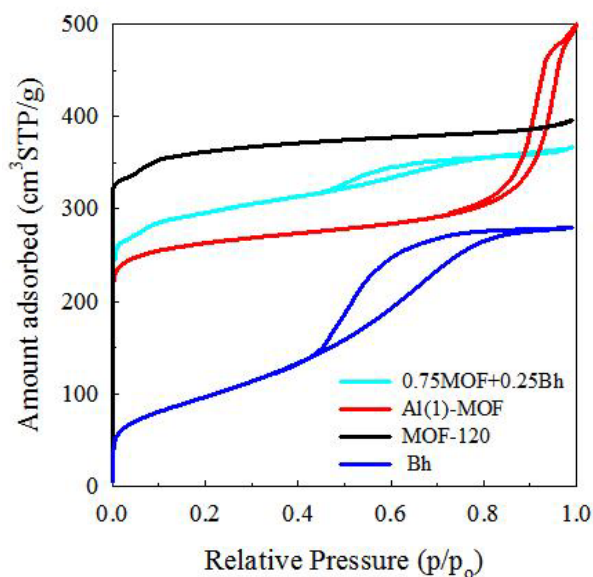


Figure S6. A comparison of nitrogen adsorption isotherms for the MOF-alumina composite (Al(1)-MOF; red curve) obtained by one-pot synthesis, physical mixture of powders (MOF and boehmite-generated alumina were mixed together to obtain a mixture of the same weight composition as that of the Al(1)-MOF composite; turquoise curve), pure MOF (MOF-120; black curve) and boehmite-generated alumina (labeled Bh; for details see Appl. Mater. Interfaces 2010, 2, 588; blue curve). This comparison shows that the physical mixture of MOF and boehmite-generated alumina powders possesses significantly smaller mesopores than those in the MOF-alumina composite obtained by one-pot synthesis.