Effects of Surface Modification on Suspension Stability of UiO-66-NH_2

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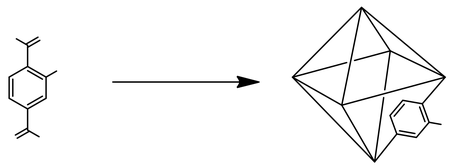
Abstract

Metal-Organic frameworks (MOFs) are a class of highly-porous, crystalline materials synthesized by bridging inorganic nodes (metal-ions or metal-oxo clusters) with multifunctional organic ligands. These materials are attractive for wide ranging applications including gas storage, separation, and catalysis, but are currently limited due to difficulties in materials handling. To try to facilitate handling of MOF powders, we have applied the process of post synthetic modification (PSM) to chemically modify the Zr-based MOF (UiO-66-NH_2) to enhance the stability of MOF suspensions in various solvents.

A range of alkyl anhydrides of different sizes were grafted to the organic portion of the MOF crystal through reaction with the free amine of the bridging ligands. Crystallinity was verified by PXRD and SEM and the reaction conversion efficiency was measured by NMR integration. These various modified MOFs were then dispersed in methanol, hexanes, water, acetone, isopropanol, DMF, and DCM to monitor the suspension stability. Most notably, dispersions of the MOFs in hexanes gained stability by this PSM method, while suspensions in water lost stability.

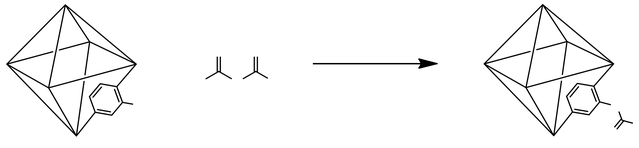
UiO-66-NH_2 Metal-Organic Framework



UiO-66-NH_2 is a Zr^{4+} based MOF with exceptional thermal and chemical stability. The parent MOF (UiO-66) has been used to great effect in the field for a wide range of catalytic and separations applications. The free amine group on the ligand allows for facile modification by standard organic chemistry techniques.

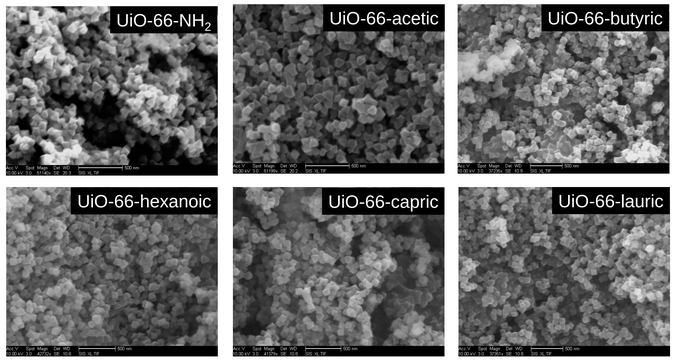
The starting material (UiO-66-NH_2) was synthesized from $ZrCl_4$ and 2-amino-1,4-benzenedicarboxylic acid (NH_2-bdc). The reagents were dissolved in N,N-dimethylformamide (DMF) and held at 120°C for 24 hrs. The resulting MOF precipitate was collected by centrifuge and washed with DMF and methanol.

PSM Reaction Scheme

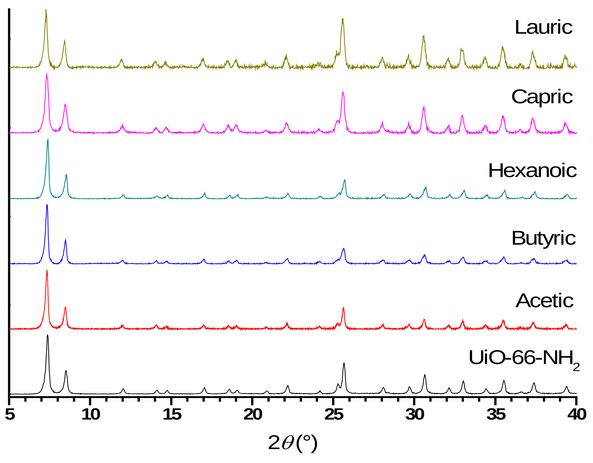


UiO-66-NH_2 powder (60 mg) was dispersed in $CHCl_3$ (2 mL) with 1 equivalent of the anhydride (acetic, butyric, hexanoic, capric, and lauric). The reagents were held at 55°C for 24 hrs. The resulting MOF precipitate was collected by centrifuge and washed with $CHCl_3$ and methanol.

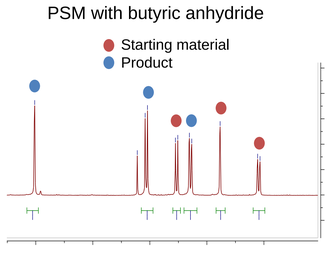
Verification of Crystallinity

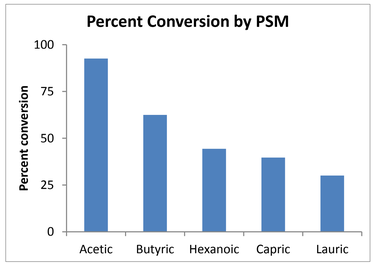


SEM. Analysis by scanning electron microscopy (SEM) reveals that the morphology of modified MOF particles remains unchanged by the PSM reaction.



PXRD. Powder X-ray diffraction (PXRD) spectra indicate preservation of the crystalline structure of the MOF after the PSM reaction.





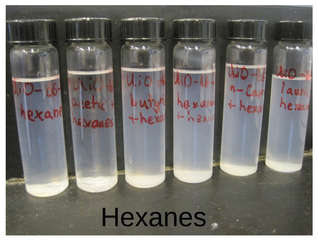
NMR. Analysis of the digested MOFs by nuclear magnetic resonance (NMR) spectroscopy allowed determination of PSM conversion efficiency by peak integration.

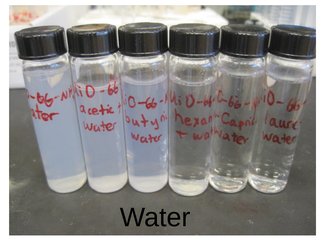
Suspension Stability

	Methanol	Hexanes	Water	Acetone
UiO-66-NH_2				
UiO-66-acetic				
UiO-66-butyric				
UiO-66-hexanoic				
UiO-66-Capric				
UiO-66-Lauric				

Poor suspension | Moderate suspension | Good suspension

Suspension stability. Use of solvents helped demonstrate how surface modification changed the stability of MOF suspensions in various solvents.





Conclusion and Future Work

UiO-66-NH_2 was synthesized and was modified through PSM with various alkyl anhydrides of varying chain length. As anhydride chain length increased, percent modification decreased. Increasing chain length added stability to MOF suspensions in nonpolar solvents (hexanes) and decreased stability in polar solvents (water). Ongoing work will seek to quantify the preliminary observations of this study and broaden the range of solvents to optimize suspension stability. We hope to use this information to facilitate handling of MOF powders for various applications.

Acknowledgements

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