FMRI RET 2017- MOF PCN-333 Synthesis for Chemical Fixation of CO_2

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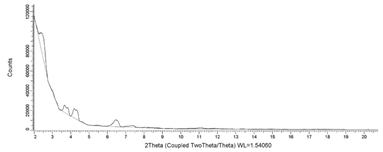
Abstract

Developing a MOF, metal-organic framework, PCN-333 with potential of holding our greenhouse gas, CO_2. Using the ligand, H_3TATB, to make PCN-333 allows the MOF to have an aluminum center. We are comparing the MOF, PCN-333, with a MOF of an iron center has shown great characteristics for CO_2 fixation using NMR, PXRD, BET, TGA and IR.

Image 1: PCN-333 PXRD



Objectives

Synthesizing the ligand H_3TATB to then synthesize the porous MOF, PCN-333, with an aluminum center that can store gas for clean energy applications.

Background

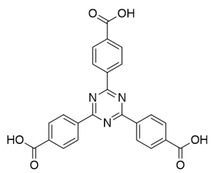


Image 2: H_3TATB Ligand

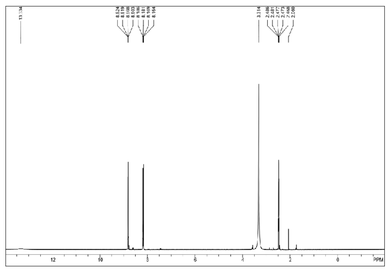
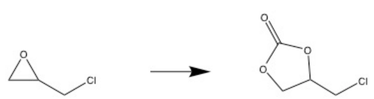


Image 3: H_3TATB NMR

Synthesis of ligand H_3TATB

p-Tolunitrile (2.9 mL) was added slowly to trifluoromethanesulfonic acid (10 g). The mixture was stirred for 13 hours, poured on ice and neutralized with ammonia water. The precipitate was collected by filtration and then washed with water and acetone. Recrystallization in toluene gave the title compound as white crystals (2.66).

Image 4: Epichlorohydrin reaction



Approach

Synthesis of ligand H_3TATB cont.

A 500 mL three-necked flask was charged with 72.64 g of acetic acid, 4.4 mL of H_2SO_4 and 2.783 g of 4,4′,4″-s-triazine-2,4,6-tri-p-tolyl. 7.2 g chromium oxide and 4.8 mL acetic anhydride were added with stirring, carefully keeping the temperature below 50° C using ice. The black-brown slurry was stirred overnight. Then the mixture was poured into 300 mL of cold water. Then we mixed and filtered. The solid was washed with water and dissolved in 200 mL 2N NaOH solution. After the unreacted starting material was removed by filtration, the solution was acidified with HCl to give basic product. Recrystallization from DMF gave a pure product as a white solid. We did this 2 times for a pure product.

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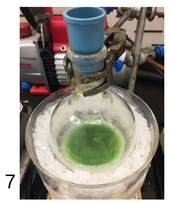

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Image 5: adding acetic anhydride while cooling with ice

Image 6:Crystallization

Image 7: Stirring over night

Synthesis of PCN-333 (Al)

When synthesizing the MOF, PCN-333 (Al), we used 50 mg of our ligand H_3TATB, 200 mg $AlCl_3$ ($6H_2O$), 10 ML of DMF, and 1 mL of trifluoroacetic acid (TFA). We dissolved the solids in DMF and sonicated for 30 minutes. We added the TFA. Next, we placed sample in a small autoclave and heated at 135 ° C for 2 days. We then filtered, exchanged in DMF and acetone 4x then dried in vacuum.

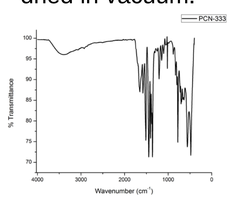


Image 8: PCN-333 IR

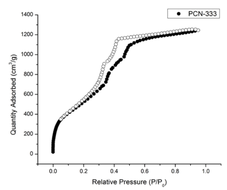


Image 9: PCN-333 BET

To polymerize inside a MOF (PCN-333)

We used 200 mg of PCN-333,100 mg of 3-ethyl-1-vinyl-1*H*-imidazol-3-ium and 4 mL of DMF. Then we stirred overnight. Next we used 25 mg of AIBN in 500 mL of DMF and added it to the reaction tube. We purged with nitrogen gas 3 times then heating it at 80 ° C, stirring for one day. After we let it cool completely we repeated the reaction letting it stir for 2 days. After filtering and washing with DMF and acetone we soaked it in acetone to remove any remaining DMF in pores. Last, we filtered and dried it in the vacuum.

Conclusions

Our reaction in image 11 was successful. Our product in the reaction tubes reacted with the CO_2 that is in the balloons. One tube has our mixture with an aluminum (Al) center and the other reaction tube has an iron (Fe) center.

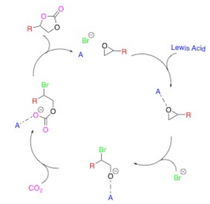


Image 10: CO_2 Reaction Cycle

Image 11: CO_2 Reaction

As you can see in our data in images 12 and 13 our reactions for PCN-333 and PCN-333-IP (with the polymer) are in sync with one another having similar peaks. With the polymer trapped inside of the MOF PCN-333 the product can now be reusable.

Image 12: PCN-333-IP TGA

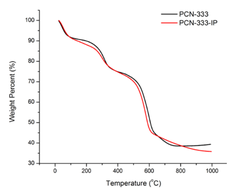
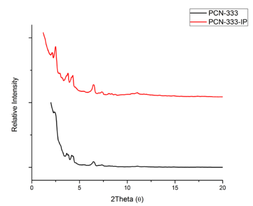


Image 13: PCN-333-IP PXRD



Referenced Resources

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2. Young Kwan Park, Sang Beom Choi, Hyunuk Kim, Kimoon Kim, Byoung-Ho Wong, Sun-Shin Cha, Young Ho Jhon, Jin Kuk Yang and Jaheon Kim; Wiley-VCH 2007 69451 Weinheim, Germany
3. Xiaodong Zou2 & Hong-Cai Zhou1,4 Nature Communication; Stable Metal-organic frameworks containing single molecule traps for enzyme encapsulation; 2015

For more information about the program visit: http://fmri-ret.eng.usf.edu/. The Research Experience for Teachers (RET) at the Functional Materials Research Institute at USF is funded by the National Science Foundation under award number 1301054.