Synthesis and studies on novel Copper adenine MOF for CO_2 adsorption

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이산화탄소 흡착용 구리 아데닌 MOF 합성 및 연구

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Abstract

A new copper adenine MOF (Bio-MOF) was synthesized by hydrothermal procedure and explored for its low temperature CO_2 adsorption. In this adenine a DNA nucleotide was used as a ligand for Cu in DMF solution at 130°C. The synthesized Bio MOF was characterized by XRD, SEM, EDS, TG and BE Tresults. The material possesses high surface area (716.08 m^2g^{-1}) with mono dispersed particles of about 2.126 nm. The maximum CO_2 adsorption capacity is 5wt% at 50 °C, which is regenerable at 100 °C which is very low when compared to other metal organic frame work studied. This study proves that the synthesized material is also be a choice materials for low temperature CO_2adsorption.

Key word: Copper, adenine, MOF, CO_2 adsorption.

1. Introduction

Among the green house gases Carbon dioxide (CO_2) is consider as a earth threatening green house gas (GHG), due the continuous utilization fossil fuel for energy production and for automotives raises its accumulation into the atmosphere. This leads to climatic change which is followed up by the destruction of earth's ecological system. But for the global energy requirement we solely depend on fossil fuel, hence it is crucial task to the scientific community to mitigate the emission CO_2 before it reaching its high concentration or finding new renewable energy source.

For the past one decade lot of adsorbents were studied for CO_2 adsorption such as mesoporous silicas, amine functionalized meso silica, zeolites, and polymeric membrane based adsorbents were studied for this purpose. Recently a wide range of metal organic frame works such as Cu-BTC, Zn-BDC, Mg-BDC, IR-MOF were successfully synthesized and studied for CO_2 adsorption. In most case they were studied at high pressure. Pressure swing studies have some demerits such as need of special apparatus for making pressure, even the pressure will break the particle if it exposed to a particular pressure continuously. Most recently the adenine bio-MOF with Cobalt was studied for CO_2 adsorption, and zinc adenine bio-MOF was also synthesized and studied for drug delivery research. As of our knowledge Cu-bio MOF was not studied for CO_2 adsorption. Hence in our present studies we portrayed the synthesis of adenine copper bio-MOF and studied for its CO_2 adsorption capability.

2. Experimental

2.1. Synthesis of Cu-adenine MOF

A stock solution of adenine (0.05 M) in N,N-dimethylformamide (DMF) was prepared by dissolving adenine in DMF by ultrasonification and heating . Similarly a stock solution of copper acetate (0.05 M) in DMF was also prepared. 7.5 mL of adenine stock solution and 2.5 mL copper

acetate t stock solution were added in to a small beaker and mixed well at 0°C in an ice bath. Then the purple solution which thus formed was then transferred into a teflon lined autoclave sealed, heated at 130 °C for 24 h, and then cooled to room temperature. The resultant purple crystals were washed with DMF and dried in air 15 min.

3. Results and Discussion

3.1. Characterization

The synthesized material was characterized by BET, TG, XRD, SEM and EDX. Powder X-ray diffraction patterns were recorded using a Rigaku Miniflex diffractometer with Cu Kα radiation (λ = 0.154 nm). The diffraction data were recorded in the 2Θ range 0.5 – 10° with 0.02° step size and 1 s step time Fig.1.This shows the high crystalinity of synthesized MOF with the presence of little Cu_2O phase.

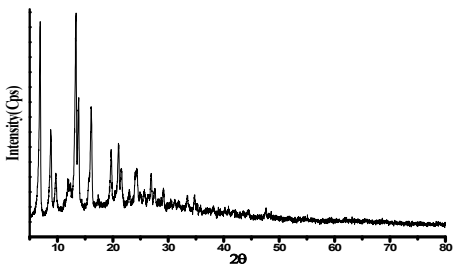

Fig.1. XRD pattern of Cu-Bio-MOF

3.2. BET

With reference to IUPAC classification of N_2adsorption – desorption isotherms, the synthesized Cu-bio-MOF (Fig.3) possess microporous structure with type-I isotherm. The BET surface area and mean pore diameter obtained by BJH method was found to be 716.08 m^2g^{-1}- and 2.126 nm respectively. The surface area is high compared to previously reported bio-MOF.

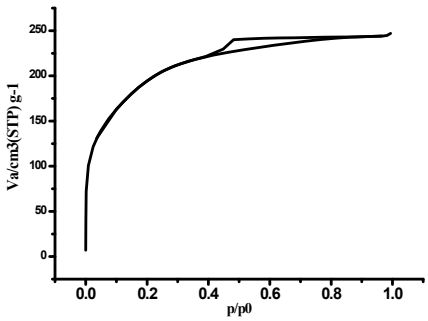

Fig.3. N_2 adsorption desorption of Cu-bio-MOF

3.3. SEM and EDX

The morphology of the synthesized material was studied using JEOL scanning electron spectrophotometer equipped with EDX system. The particles are with cube crystal morphology (Fig.3.). The presence of Cu, C, N_2 is evidenced from the EDX analysis and was found to be about 10.17 % wt of copper present in the MOF (Fig 3a, b).

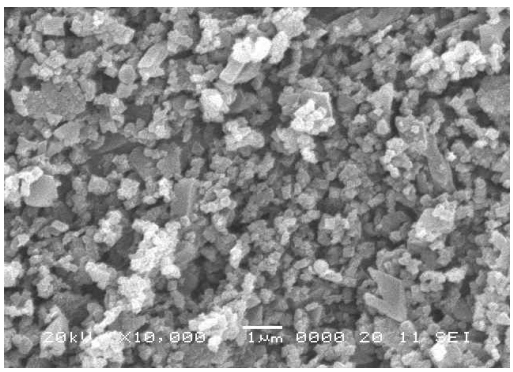

Fig 3(a) SEM micrograph of Cu-bio MOF

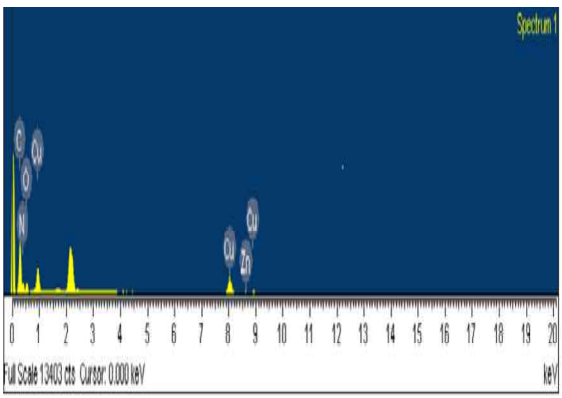

Fig 3(b) EDS results of Cu-bio MOF

3.4. TGA

SCINCO thermo gravimeter N-1000 was used for these studies. The TG result is similar with already reported Co-Bio MOF which showed a 20 % weight loss at 200°C due to loss of water and DMF guest molecule. The weight loss after 200 °C was attributed for template removal from the MOF(Fig.4).

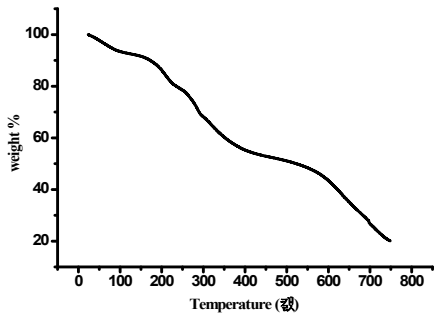

Fig.4. TG results of Cu-bio-MOF

3.5. CO_2 adsorption

CO_2adsorption – desorption measurements of the synthesized material was performed on thermo gravimetric analyzer (SCINCO thermo gravimeter N-1000). The adsorption run was carried out using high purity CO_2 (99.9%) gas at 25°C under atmospheric pressure while the regeneration was carried out under N_2 flow at 100°C. A sample weight of ca. 10mg was loaded in to an alumina sample pan in a TG unit and initial activation was carried out at 100°C for 1 h in nitrogen atmosphere. Continuous CO_2 adsorption – desorption profile was obtained by heating, cooling and changing the gases CO_2 (99.9%) and N_2 through automatic switching valve assisted with timer. A feed flow rate of 30ml/min was controlled by a MFC to the sample chamber in TG unit. CO_2 adsorption result shows an adsorption capacity of 5wt% (Fig.5.) and remained the same even up to 3 repeated cycles (figure not shown).

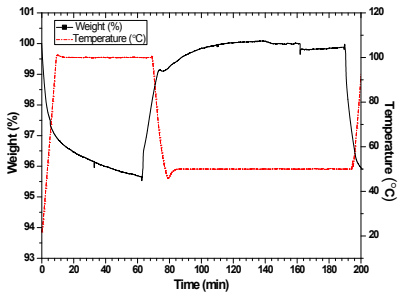

Fig. 5. CO_2 Adsorption, desorption by Cu-bio-MOF

4. Conclusions

We successfully synthesized Cu-adenine bio-MOF by hydrothermal procedure. The XRD pattern proves the crystalinity of the complex produced. The SEM-EDS results confirm the presence of Cu-in the formed MOF and the crystalline morphology of prepared MOF. The maximum adsorption capacity of the MOF was found to be 5 wt%. Further studies on material such as crystallographic analysis and CO_2 adsorption isotherm were undergoing to standardize the complex.

5. Acknowledgements

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References

[1] J .S Beck , J. C Vartuli, W. J Roth, M. E Leonowicz, C.T Kresge, K. D Schmitt, C. T. W Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, J. Amer. Chem. Soc., 1992,**114(27)**, 10834.

[2] A. Monnier, F. Schuth, Q. Huo, D. Kumar, D. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke, B. F.Chmelka, Science, 1993, **261(5126)**,1299.

[3] S. Hao, Q. Xiao, H. Yang, Y. Zhong, F. Pepe,

W. Zhu,Micro. Meso. Mater., 2010,132(3), 552.

[4] H. Yoshitake, E. Koiso, H. Horie, H.Yoshimura ,Micro. Meso. Mater., 2005,85(1-2) , 183-194

[5] J.A. Dunne, M. Rao, S. Sircar, R.J. Gorte, A.L. Myers, Langmuir, 1996,12 , 5896 – 5904.

[6] C. A. Scholes, K. H. Smith, S. E. Kentish, G. W. Stevens, Int. J. Greenh. Gas. Con., 2010, 4(5), 739.

[7] M. Eddaoudi, H.L. Li, O.M. Yaghi, J. Am. Chem. Soc., 2000,122,1391.

[8] M. Eddaoudi, D.B. Moler, H.L. Li, B.L. Chen, T.M. Reineke, M.O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319.

[9] S. Kaskel, in: F. Schuth, K.S.W. Sing, J. Weitkamp (Eds.), Handbook of Porous Solids, Wiley-VCH, Weinheim, 2002, 1190.

[10] O.M. Yaghi, H.L. Li, C. Davis, D. Richardson, T.L. Groy, Acc.Chem. Res. (1998), 31, 474.

[11] J .Liu, J. Y. Lee, L. Pan, R. T. Obermyer, S. Simizu, …B. Zande, J. Li, S. G Sankar, J. K . Johnson, J . Phy. Chem. B (2008), 112(8) , 2911.

[12] S.W. Krista, R. M. Andrew, D. David, H. Frost, J. L. John,O. M. Yaghi, R.Q. Snurr,**J.Am.Chem.Soc.(2008)**,130,406.