

## Stability Study on Amine-Functionalized MIL-101 for CO<sub>2</sub> Capture

Sanjit Gaikwad and Sangil Han\*

Department of Chemical Engineering, Changwon National University,  
Changwon, 51140 South Korea

\*Corresponding author, e-mail shan@changwon.ac.kr

### INTRODUCTION:

The increasingly intensified environment perdition problem induced by greenhouse gas (GHG) effects has received great attention. Greenhouse gasses mainly consists of methane (CH<sub>4</sub>), H<sub>2</sub>O, nitrous oxide (N<sub>2</sub>O), CO<sub>2</sub>, etc., among which CO<sub>2</sub> occupy 55% and makes a great contribution to the GHG effect.[1] The increasing atmospheric CO<sub>2</sub> concentration and its impact on the environment have led to increasing attention directed toward finding advanced materials/technologies suitable for efficient carbon capture and storage [2] while improving the efficiency of energy utilization and increasing the use of low-carbon energy sources are potential ways to reduce CO<sub>2</sub> emissions . The Intergovernmental Panel on Climate Change (IPCC) pointed to anthropogenic CO<sub>2</sub> as a major contributor of global warming and climate change which is now considered as a global problem. Thus, the challenge of reducing CO<sub>2</sub> emissions has become a crucial issue for the 21st century, leading to the expansion of renewable technologies, energy saving and carbon capture and sequestration (CCS). The CCS technology is an effective way to reduce CO<sub>2</sub> emissions [3]which includes four steps: CO<sub>2</sub> capture, compression, transportation and storage, while the cost for CO<sub>2</sub> capture accounts for about 75% of the total cost for CCS process. The most important factor is to develop cost-effective techniques for the capture and separation.

Research on metal–organic frameworks (MOFs) and/or coordination polymers is certainly one of the most active research fields among chemistry and materials community, as witnessed in a large number of publications.[4] MOFs now can be conventionally designed and constructed from a large number of metal ions and/or metal-containing clusters, and organic ligands through very straightforward solvothermal synthesis approach, and their structures can be routinely characterized by laboratory X-ray, synchrotron, and/or neutron diffraction studies[5] can also be considered as organic/inorganic hybrid materials. That has provided us the bright promise of making use of inherent porosities, and physical and chemical properties of inorganic metal nodes, organic building blocks and encapsulated species inside the pores to target a variety of functional MOF materials. The most utilized application of MOFs is adsorption, which can be carried out for different purposes. These include the removal of harmful materials from liquid/gas phases, gas storage, separation, purification, catalysis, drug delivery and so on. In every case, the applicability and performance of an MOF can be improved by forming a composite with suitable MOFs, mainly because of the imparted functionality and enhanced porosity. Specially, in such cases where selective adsorption or separation is necessary, MOF composites can show spectacular effects. MOF composites can be applied in every field where MOFs can be applied, and additional new possibilities can also be found in applications where individual MOFs cannot be used. With suitable functional materials, limitless composites are bound only by one's imagination, and can be prepared for new applications.

The CO<sub>2</sub> capture performance can be improved by introducing a functional group with affinity for CO<sub>2</sub> (e.g., amine group) into a structure of nanoporous material because the introduction of basic amine groups into pore structure of a nanoporous support can lead to a composite solid material with the preferential adsorption of weakly acidic CO<sub>2</sub>. Solid amine adsorbents developed by amine species loaded on certain carrier materials are widely investigated. Son et al. [6] studied polyethyleneimine (PEI)-loaded SBA-15, SBA-16, and KIT-6 mesoporous molecular sieves as well as the CO<sub>2</sub> adsorption performance of the modified adsorbents. The optimal sorbents were SBA-16 and KIT-6, with adsorption capacities of 2.93 and 3.1 mmol/g, respectively. Chen et al. [7] prepared monolith silica with Hierarchical pore structure and tested a CO<sub>2</sub> capturing sorbent after amine impregnation and they reported 4.77mmol/g CO<sub>2</sub> Adsorption capacity at 75 °C temperature and 1 bar pressure. Subagyono et al. [8] reported a PEI-impregnated mesocellular siliceous foam (MCF) for CO<sub>2</sub> capture that had a large pore volume (2.5 cm<sup>3</sup> /g) and pore size (31 nm). The adsorption capacity of MCF loaded with PEI reached 151 mg/ g adsorbent in 20 min adsorption time at

temperature 105 °C and pressure 0.5 atm.

In this work we developed PEI impregnated Cr and Mg bimetallic MOF (MIL-101 (Cr, Mg) by using a wet impregnation method to enhance CO<sub>2</sub> capture performance. It was reported that MIL-101(Cr, Mg) possesses relatively large surface area of 3274 m<sup>2</sup>/g, excellent stability to chemical, heat and moisture, and increased CO<sub>2</sub> sorption capacity compared to parent MIL-101 (Cr) due to open metal site and alkaline group.

## 2. Experimental:

### 2.1 Sample preparation:

#### a) MIL-101(Cr):

MIL-101 was synthesized by hydrothermal method according to the well documented procedures [9] and briefly described here. A mixture of Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (1.2 g, 3 mmol), terephthalic acid (H<sub>2</sub>bdc, 500 mg, 3 mmol), and HF (5 M, 0.6 mL, 3 mmol) in H<sub>2</sub>O (15 mL) was heated in a Teflon-lined stainless-steel autoclave at 493.2 K for 8 h. Solvent removed by using centrifuge at 5000 rpm speed. After cooling the precipitate was centrifuged and washed with five times with 200ml of hot water (333K) to remove NH<sub>4</sub>F [10]. Finally, the as-synthesized MIL-101(Cr) was dried at 373 K and then evacuated at 423 K for 12 h.

#### b) MIL-101(Cr, Mg):

MIL-101(Cr, Mg) was synthesized by hydrothermal method according to the literature [11]. Chromium nitrate (4.0g,10mmol) terephthalic acid (1.64 g,9.87 mmol), deionized water (48mL) and HF solution(40%,0.33mL) were mixed in a Teflon autoclave reactor and stirred at 313K for 10 min, and then magnesium nitrate hexahydrate (0.238g,1mmol) was added into the mixture. The autoclave reactor was sealed in stainless steel vessels and the temperature was increased from 40°C to 220°C for 40 min, and incubated for 8 h, followed by cooling to 160 °C for 3 h, cooling to 90°C for 3 h, and cooling to 35 °C for 6 h. Green powders were obtained as a major product.

#### c) PEI-impregnation on MIL-101 (Cr, Mg):

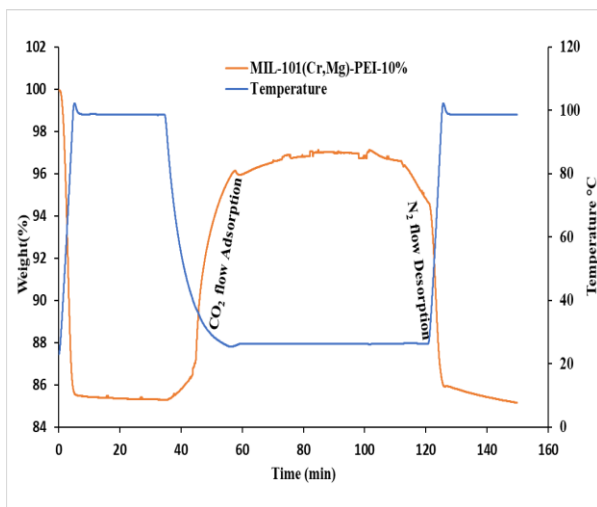
The PEI-MIL-101(Cr, Mg) adsorbent was prepared by wet impregnation method. Polyethyleneimine (PEI branched type, average molecular weight 600, density = 1.05 g/mL) from Sigma–Aldrich was used for impregnation in MIL-101 (Cr, Mg). Before the impregnation, the MIL-101 (Cr, Mg) powders were heated at 160 °C under vacuum condition for 4hrs to evacuate the samples. The desired amount of PEI (5-40%) was dissolved in 4 mL anhydrous methanol under stirring for 10 min at temperature 40 °C [12,13] and then 0.2 g MIL-101 (Cr, Mg) were added step by step into the PEI/methanol solution under stirring.

### Characterization of CO<sub>2</sub> sorbents:

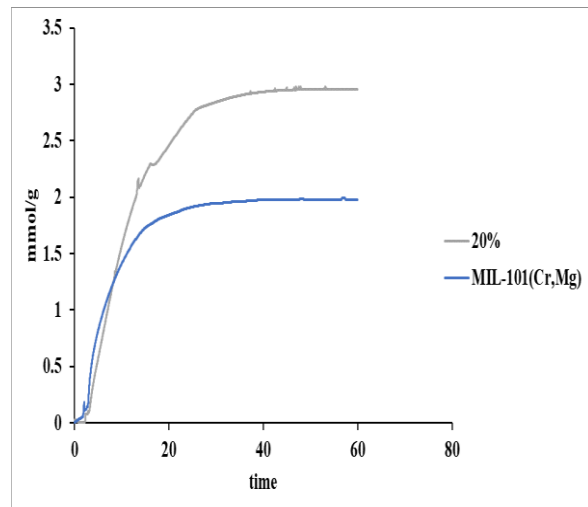
For the crystal structure identification, XRD was measured after sample activation on 90°C for 3hrs. Scanning electron microscopy (SEM) was used to observe the samples morphology. Measurements were made using an accelerating voltage of 1 kV/10 kV and 10 μA current. The isotherm of adsorption-desorption was obtained at liquid nitrogen temperature 77 K by using of the principle of physical adsorption of N<sub>2</sub>. Before N<sub>2</sub> adsorption–desorption test, the adsorbents were vacuum-treated for 4 h at 100 °C. The specific surface area of these samples was determined at a P/P<sub>0</sub> close to 0.999 using the Brunauer–Emmett–Teller (BET) method. The total pore volume was estimated from the adsorbed capacity of N<sub>2</sub> at a relative pressure. BJH method used to determine the pore size distribution.

## RESULTS AND DISCUSSION:

Fig.1 show the CO<sub>2</sub> adsorption of MIL-101(Cr,Mg)-PEI-10% and Fig.2 represent CO<sub>2</sub> adsorption in mmol/g. For the PEI impregnated MOFs, TGA was used to measure capacities showing that the capacity and selectivity increased with PEI increase.

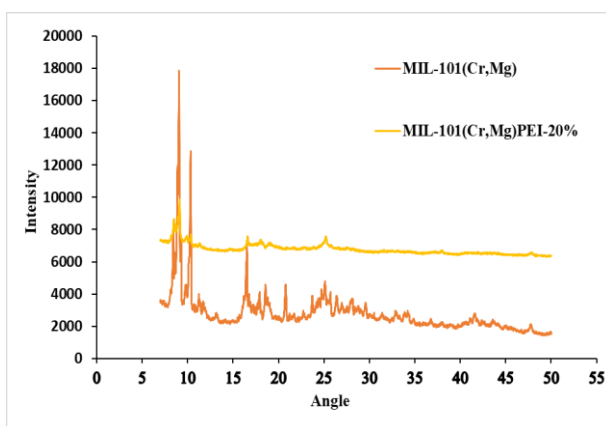


**Fig.1** TGA CO<sub>2</sub> Adsorption of MIL-101(Cr, Mg)-PEI-10%

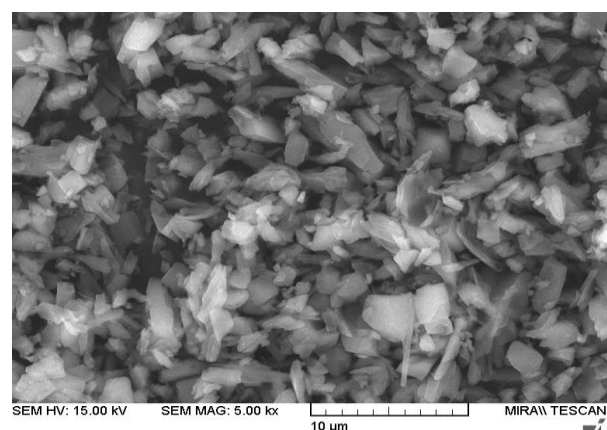


**Fig.2** CO<sub>2</sub> Adsorption of MIL-101(Cr, Mg)-PEI-20 and MIL-101(Cr, Mg) in mmol/g.

CO<sub>2</sub> adsorption at 1 bar was measured with a thermogravimetric analyzer. The weight changes of the adsorbents were recorded to determine CO<sub>2</sub> adsorption capacities. 10 mg of the adsorbent was placed in a sample pan, then heated to 100 °C with a rate 20 °C /min during N<sub>2</sub> gas purging at a flow of 50 cc/min and hold at that temperature for 1 h until no weight loss was observed. The temperature was then adjusted to the desired temperature. Finally, ultrapure CO<sub>2</sub> was introduced at a flow rate of 50 cc/min for 60 min. The uptake of CO<sub>2</sub> on the MIL-101 (Cr, Mg)-PEI was determined based on the mass increase during the adsorption stage. In case of MIL-101(Cr, Mg)-PEI, CO<sub>2</sub> adsorption capacities increases with increase in PEI % up to 10% and from 10% it start decreasing. Fig.3 Represent XRD MIL-101 (Cr, Mg) and MIL-101 (Cr, Mg)-PEI-20%. From XRD Fig it is clear that Intensity of peak decrease as well as some peak disappear with increase in PEI percentage.



**Fig.3** XDR of MIL-101(Cr, Mg) and MIL-101(Cr, Mg)-PEI-20%



**Fig.4** SEM of MIL-101(Cr, Mg)-PEI-20%

## CONCLUSION:

Low CO<sub>2</sub> adsorption capacity MOF MIL-101(Cr) doped with Mg. CO<sub>2</sub> adsorption capacity of MIL-101(Cr, Mg) increased by 20% than the parent MIL-101(Cr). Further the capacity of MIL-101(Cr, Mg)

increased 50% by impregnation with PEI(Mw-800).As percentage of PEI increased pore volume as well as surface area decreased. Due to decrease in surface area and pore volume CO<sub>2</sub> adsorption capacity decreases. After PEI impregnation there is no significant effect on particle size because PEI impregnated inside the pore and unreacted PEI was removed by ethanol washing. Stability of MIL-101(Cr,Mg) confirmed by exposing this material in humid air and acid gases. After Humid air exposure and SO<sub>x</sub> and NO<sub>x</sub> exposure there is no significant effect on its CO<sub>2</sub> adsorption capacity.

## Reference:

- 1 Cox, P. M.; Betts, R. A.; Jones, C. D.; Spall, S. A.; Totterdell, I. J. Nature 2000, 408, 184–187.
- 2 Haszeldine R. S. Science, 2009,325, 1647.
- 3 S.S. Lee, S.M. Mun, W.J. Choi, et al., Environ. Sci. 2012,24 897-902.
- 4 Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M Science 2013, 341, 123044.
- 5 Zhou, H.-L.; Zhang, Y.-B.; Zhang, J.-P.; Chen, X.-M. Nat. Commun. 2015, 6, 6917.
- 6 Son, W. J.; Choi, J. S.; Ahn, W. S. Microporous Mesoporous Mater. 2008, 113, 31–40.
- 7 C. Chen, S. T. Yang, W. S. Ahn and R. Ryoo, Chem. Commun., 2009,3627.
- 8 D. J. N. Subagyono, Z. Liang, G. P. Knowles and A. L. Chaffee, Chem. Eng. Res. Des., 2011,89, 1647.
- 9 Z. Saedi, Sh. Tangestaninejad, M. Moghadam, V. Mirkhani and I. Mohammadpour-Baltork, Catal. Commun., 2012, 17, 18.
- 10 Philip L. Llewellyn, Sandrine Bourrelly, Christian Serre Langmuir 2008, 24, 7245-7250.
- 11 Zhenyu Zhou, Liang Mei, Chen Ma Chemical Engineering Science 2016,147, 109–117.
- 12 Sung S., Paik M... J. Mater. Chem. A, 2014,2, 13245.
- 13 Zhenyu Z, Liang M, Chen Ma, Feng Xu, Chemical Engineering Science, ,2016,147,109-117.