MOF의가스흡착능력및수분, 산성가스에대한안정성연구

한상일, J. Carson Meredith*
창원대학교화공시스템공학과, 조지아텍화학공학과*

Adsorption of CO_2, N_2, and SF_6 on MOFs with study on stability to humid air, liquid water and acid gases

Sangil Han, J. Carson Meredith*
Department of Chemical Engineering, Changwon National University,
School of Chemical & Biomolecular Engineering, Georgia Institute of Technology*

Introduction

There have been increasing research efforts on separation of CO_2 from flue gas to alleviate global warming effects. The CO_2 emission comes predominantly from the burning of oil, coal, and natural gas and, and is anticipated to continue to rapidly increase due to economic growth. In the period of 1958-2010, the CO_2 concentration in the atmosphere has increased from 280 to 390 ppm with accelerating increase [1]. The increased CO_2 concentration has been known to be responsible for the increased surface temperature of the earth by disturbing the balance of incoming and outgoing energy in atmosphere system, resulting in the climate change. Therefore, it is critical to reduce the CO_2 emission for the sustainable development.

Current adsorption technologies based on chemical adsorption, which involve amine solutions to selectively capture CO_2 in flue gas, suffer from high energy penalty which is approximately 30% of the power generated at power plant [2]. The majority of the energy cost stems from the regeneration of the sorbent (amine solution) as high temperature is required to break the amine-carbon dioxide chemical bonds.1 Furthermore, the regeneration process caused irreversible solvent loss and degradation due to the high temperature [3]. In this concern, there are critical needs to discover and develop new capture materials as physical sorbents which circumvent regeneration and solvent loss, leading to energy-efficient process over the amine-based chemical adsorption systems [4].

In recent years, much attention has been focused on metal organic frameworks (MOFs) [5], a new class of nanoporous materials with high surface area and well-defined pore structure, due to their potential applications in separation, catalysis, and gas storage. There is almost unlimited number of potential MOFs asMOFs are synthesized with various combinations of organic linkers and metal joints, providing an opportunity to tailor surface area, pore size, and surface functionality. However, so far a few MOFs have been reported with their adsorption properties6 without considering stability problems. Furthermore most studies have focused on adsorption of only a few MOFs at a time [5], limiting rapid characterization of MOFs for CO_2 separation in a huge library.

In this study, we presented adsorption properties of CO_2 and N_2 for seven MOFs by using the high-throughput (HT) sorption system.7 Additionally, stability to humid air, liquid water, short-term and long-term exposure to acid gases was investigated as post-combustion flue gas is composed of H_2O, SOx, NOx, etc [2]. Flexibilities of the MOF frameworks were examined by measuring SF_6 adsorption on the MOFs in order to verify rigid structures which effectively exclude gas molecules with at least 5.6 Å of SF_6 kinetic diameter.

Materials

Eight MOFs were synthesized for this study following the synthesis procedures {CdZrSr(C2O4)4·6H2O}n (CdZrSr), {[Ni2(NIC)4(μH2O)] ·CH3CH2OH·H2O}n (Ni-NIC), {[LnCu(nic)2(C2O4)] ·xH2O}n (La-Cu), {[EuCu(NIC)2(C2O4)] ·xH2O}n (Eu-Cu), {[Zn2(2,6-ndc)2(bpy)]}n Zn-NDC, {(C6H14N)2[Zn3(HPO3)4]}n (ZnPO3), {Cu(hfipbb)(H2hfipbb)0.5}n (Cu-HF), and Cu-NH2. Most MOFs showed negligible Brunauer−Emmett−Teller (BET) surface areas measured from N_2 physisorption at 77 K, which range 0 - 53 m_2/g due to pore limiting diameters8

(PLD) of the MOFs smaller than the nominal kinetic diameter of N_2, resulting in strongly hindered diffusion of N_2 into the pores at low temperature, 77 K.

Adsorption Measurements

The adsorption amounts of the MOFs were measured by using the HT sorption system, which monitors pressure change as a function of time in each sample chamber, under a low pressure less than 1 atm at 30 °C. 50 mg of MOFs were loaded. The MOFs were activated at 180 – 200 °C for 20 hours under vacuum prior to measurements. Between the measurements, samples were degassed for 5 hours under vacuum at room temperature. The measurements were repeated in triplicate to provide reliability. The operations including valve on-off for 80 ms and data acquisition were achieved using LabVIEW.

Stability Test

The MOFs were exposed to 15 ppm of SO_2 for 2 – 5days and 15 ppm of NO_2 for 2 - 5 days under humid air (80% relative humidity) at 27 °C which were prepared using salt solutions according to the literature [9]. The 15 ppm of SO_2 gas was generated with a 500 μg/ml $NaHSO_3$ aqueous solution with pH 3.7 at 45 °C. 200 ml/min of air flow transferred the generated SO_2 gas from reaction tube into a desiccator which has 80% relative humidity prepared with a saturated NaCl solution. 10 ppm of NO2 gas was generated by using the same apparatus with a different condition (800 μg/ml of NaNO2 aqueous solution with pH 3 at 45 °C with 100 ml/min of air flow). Gas concentrations were verified with Dräger-Tubes (Dräger, Germany) where a chemical reagent reactive to a specific gas is filled in the tube. We further investigated the stability of MOFs with liquid water. Deionized water was dropped onto each MOF in the sample chamber of the HT sorption system and then MOFs were left for 2 days at room temperature. The MOF samples were evacuated at 130 °C under vacuum for 20 hours after the exposure prior to the adsorption measurements.

Results and discussion

The adsorption was measured at 30 °C under low equilibrium pressures, 3 – 10 psi for CO2 and 9 – 12 psi for N2 depending adsorption capacities of MOFs while initial pressure of 14 psi was injected to each sample chamber. The adsorption capacities were obtained from the average values after reaching at equilibrium state of the adsorption kinetics. In particular, Cu-HF, Zn-NDC, and Ni-NIC showed relatively high CO2 uptake capacities than the other MOFs. Adsorption reached at equilibrium after 0.2 hour for CO2 and N2. Because the adsorption capacities obtained from the average values at time (0.5 - 0.8 h), were measured at low pressures less than 1 atm, the adsorption selectivity is a ratio of the Henry's constants for CO2 and N2, assuming that adsorption is in Henry's regime. To assess the stability to humid air and acid gases, the MOFs were exposed to humid air with 80% relative humidity for 3 days, SO2 for 2 days and NO2 for 2 days under humid air with 80% relative humidity, respectively.

The adsorption capacities were measured in three different conditions, before humid air, after humid air and after acid gases with humid air in order to understand the effects of humid air and acid gases on adsorption capacities. Henry's constants were used to compare the adsorption capacities obtained at different equilibrium pressures. Cu-HF, Zn-NDC, and Ni-NIC showed relatively high CO2 and N2 uptakes compared to the other MOFs. There were no noticeable changes after humid air exposure and after acid gases exposure except Cu-HF and Ni-NIC. Adsorption amounts increased for Cu-HF and decreased for Ni-NIC during the exposure to humid air and acid gases while similar XRD patterns were observed for the most MOFs after humid air and acid gases exposure, indicating that the humid air and acid gases had no effects on their original crystal structures. However, the XRD of Cu-HF showed peak disappearance at 8.4 ° and peak intensity and width changes at 12 – 15 ° after humid air exposure.Sorption selectivities appeared to be 8 for Cu-HF and Zn-NDC and 8 - 12 for Ni-NIC in the range of those for ZIF-90, ZIF-8, ZIF-7, and Zn-TTC in previous study7. Relatively low adsorption selectivities, ~4, were observed for Eu-Cu, ZnPO3, La-Cu, and CdZrSr mainly due to the very low CO2 adsorption capacities compared to the other MOFs.

Diffusion selectivities for the MOFs were estimated by using a micropore diffusion model [10] assuming a mass transfer resistance primarily due to intracrystalline diffusion. Adsorption kinetic graphs where uptake amounts are between 70 – 90% were used to estimate diffusivities and diffusion selectivities. The diffusion selectivities appeared between 2 and 3.5 for Cu-HF, Zn-NDC, CdZrSr, and Ni-NIC while Eu-Cu, ZnPO3, and La-Cu showed low diffusion selectivities around 1. Diffusion selectivity decreased for ZnPO3 after humid air exposure and increased for CdZrSr after humid air exposure. Small changes in XRD peak intensity for ZnPO3 and peak width for CdZrSr were observed after humid air exposure compared to the XRD of activated samples.

We further examined long-term stability to SO2 and NO2 gas exposure for the Zn-NDC, Cu-HF, and Ni-NIC which showed higher sorption selectivities than other MOFs. The MOFs were exposed to SO2 for 5 days, and then exposed to NO2 for 5 days under humid air with 80% relative humidity. Adsorption capacities of CO2 and N2 were measured and XRD patterns were taken after exposure to each acid gas. Ni-NIC showed increased CO2 and N2 adsorption capacities after the long-term SO2 exposure for 5 days (Figure 1). The similar behavior was observed after the humid air exposure and the short-term SO2 and NO2 exposure. CO2 adsorption decrease by 30% on Zn-NDC resulted in decrease on adsorption selectivity from 14.3 to 11.1 after the long-term NO2 exposure for 5 days. Partial decomposition of the original structure in Zn-NDC was confirmed by XRD patterns which showed peak disappearance and reduced peak intensity after the long-term NO2 exposure with humid air for 5 days. There were no noticeable changes in XRD patterns for Ni-NIC and Cu-HF.

In practical applications with flue gas, water condensation could happen in adsorbents and affect the performance of adsorbents. Thus, we additionally investigated the MOFs stability to liquid water. Adsorption capacities were measured and XRD patterns were taken before and after liquid water exposure for 2 days at room temperature. Ni-NIC and Cu-HF were stable in liquid water exposure, which presented similar adsorption capacities and XRD patterns before and after the liquid water exposure. However, Zn-NDC showed decreased CO2 uptake by 26.5% and significantly reduced peaks in XRD pattern at 9.8, 13.7, 14.5, 16.3, 17.9 and 21 ° while the water vapor exposure on Zn-NDC showed no decrease in uptake capacities with reduced XRD peak intensities at 9.6, 17.8 and 21 ° after the humid air exposure.

Framework flexibility of Cu-HF, Zn-NDC, Ni-NIC, and Cu-NH2 was examined by using SF6 gas adsorption. The adsorption capacities of SF6 appeared 70 – 80% lower than those of N2 as the small pores (2.6 – 3.2 Å) of the MOFs limit the transport of the SF6 molecules with 5.5 Å of kinetic diameter into the frameworks of the MOFs, indicating that the frameworks of the MOFs remain rigid at the experimental condition (30 °C and 9 – 12 psi).

Conclusions

7 MOFs were characterized to identify sorption and diffusion selectivities of CO2/N2 using the HT sorption measurement apparatus with stability evaluations to humid air, acid gases and liquid water. Sorption selectivities for Cu-HF, Zn-NDC, and Ni-NIC were similar to those for ZIFs and Zn-TTC, however lower than Co-NIC and Cu-PCN. In the long-term acid gas exposure and the liquid water exposure, the original framework structures of Cu-HF and Ni-NIC remained stable with no decrease in adsorption capacity. However, according to the XRD patterns Zn-NDC showed partial decomposition of the original frameworks with decrease in CO2 sorption capacity by 26 – 30% (sorption selectivity decrease from 14 to 11 after the long-term NO2 exposure for 5 days and the liquid water exposure. The limited adsorption capacities of SF6 compared to N2 adsorption suggested no large flexibility of the MOF frameworks as the rigid frameworks hinder the SF6 diffusion into the pores due to the large size difference between SF6 and pore.

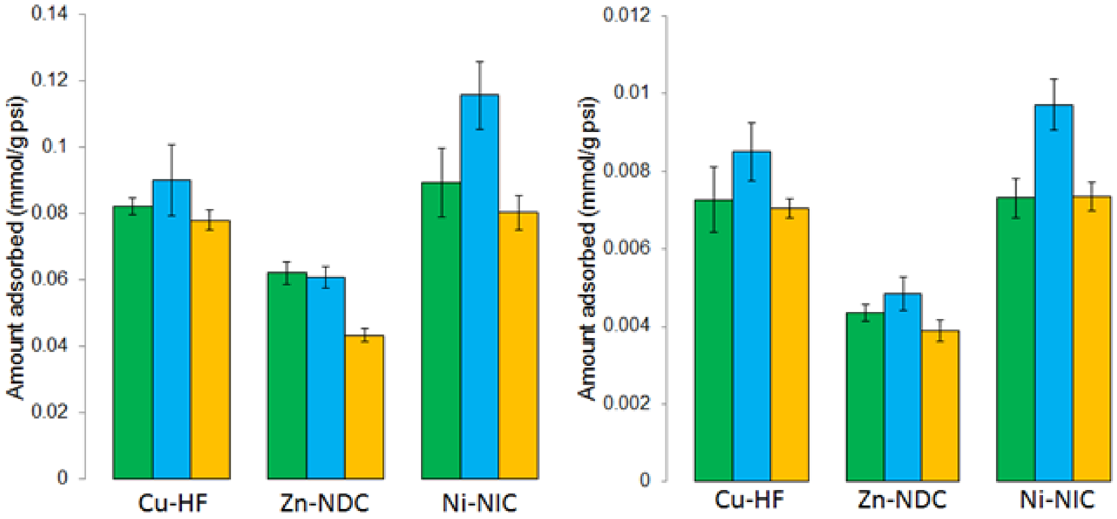

Figure 1. CO2 (a) and N2 (b) adsorption capacities measured at 30 °C after long-term exposure to acid gases. Green (before exposure), blue (after SO2 exposure with humid air), yellow (after NO2 exposure with humid air). Error bars represent standard deviation (n = 3).

References

1.J.-R.Li, Y.Mab, M. C.McCarthy, J.Sculleya, J.Yu, H.-K.Jeong, P. B.Balbuena, H.-C.Zhou, Coord. Chem. Rev.,255, 1791 (2011).

2.K.Sumida, D. L.Rogow, J. A.Mason, T. M.McDonald, E. D.Bloch, Z. R.Herm, T.-H.Bae, J. R.Long, Chem. Rev., 122, 724 (2012).

3. J. Tan, H.Shao, J.Xu, L.Du, G. Luo, Ind. Eng. Chem. Res., 50, 3966 (2011).

4. A.Samanta, Zhao, A.; Shimizu, G. K. H.; Sarkar, P.; Gupta, R. Ind. Eng. Chem. Res. 51, 1438 (2012).

5. S.Keskin, T. M. v.Heest, D. S.Sholl, ChemSusChem, 3, 879 (2010).

6. A. O.Yazaydın, R. Q.Snurr, T.-H.Park, K.Koh, J.Liu, M. D.LeVan, A. I.Benin, P.Jakubczak, M.Lanuza, D. B.Galloway, J. J.Low, R. R.Willis, J. Am. Chem. Soc., 131, 18198 (2009).

7. S.Han, Y.Huang, T.Watanabe, Y.Dai, K. S.Walton, S.Nair, D. S.Sholl, J. C.Meredith, ACS Comb. Sci., 14, 263−267 (2012).

8. E.Haldoupis, S.Nair, D. S. Sholl, J. Am. Chem. Soc., 132, 7528 (2010).

9. Y.Hashimoto, S. Tanaka, Environ. Sci. Technol.,14, 413 (1980).

10. Z.Bao, L.Yu, Q.Ren, X.Lu, S. Deng, J. Colloid. Interface Sci., 353, 549 (2011).