

# Effects of amino functionalization on Zr-based MOFS for methane and carbon dioxide adsorption

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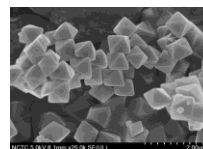
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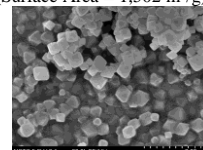
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**1. Introduction** – Greenhouse gas (GHG) emission from fossil fuel burning is one of the major problems of global warming. Natural gas is an alternative energy with lower GHG emission. One of the challenges for natural gas storage is its low volumetric density. Adsorbed natural gas (ANG) technology has attracted great attention since it increases volumetric density by filling adsorbents in the storage tank. There are many wide range of porous materials for ANG technology, but the most interesting and suitable porous adsorbents is metal organic frameworks (MOFs). This work investigated Zr-based MOFs such as UiO-66 and UiO-66-NH<sub>2</sub> for methane and carbon dioxide adsorption. In addition, the amount of amino organic linker was varied to study the degree of functionalization on UiO-66 on the adsorption of these two gases.



**Image 1.** SEM of UiO-66  
(Surface Area = 1,502 m<sup>2</sup>/g)



**Image 2.** SEM of UiO-66-NH<sub>2</sub>  
(Surface Area = 1,204 m<sup>2</sup>/g)

**2. Experimental** - All adsorbents were synthesized using solvothermal condition. The products were characterized by Fourier-transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), X-ray powder diffraction (XRD) and N<sub>2</sub> adsorption-desorption isotherm. The methane and carbon dioxide adsorption were obtained in the static process. For gas adsorption, about 0.3 g of adsorbent was weighted and degassed by using a rotary vacuum pump prior to the methane or carbon dioxide adsorption. The temperature was controlled at 33 °C with a pressure range of 0-100 psia. The gas pressure was recorded before and after each gas expansion.

**3. Results and Discussion** – The characterization shows that adding amino group on UiO-66 did not affect the crystalline structure, but decreased 20% of the surface area (Image 1 and Image 2). In general, it was found that all adsorbents had higher selectivity towards carbon dioxide than methane because the carbon dioxide molecule had dipole-quadrupole interaction with Lewis sites on the adsorbent surface. Moreover, methane and carbon dioxide adsorption on UiO-66-NH<sub>2</sub> (at 100% loading of amino group) was the highest followed by UiO-66-NH<sub>2</sub> 25%. UiO-66-NH<sub>2</sub> 75% had higher carbon dioxide capacity than UiO-66; however, it had lower methane adsorption than UiO-66. UiO-66-NH<sub>2</sub> 50% displayed the lowest methane and carbon dioxide uptake. It seems that the adsorption of carbon dioxide required functionalized organic linker, high surface area, and proper open metal site. Similarly, methane adsorption also preferred high surface area, high porosity, and functionalized organic linker to increase interaction of molecule via van der Waal force.

**4. Conclusions** – The addition of amino group increased methane and carbon dioxide adsorption despite of the decreased surface area. There was an optimum loading amino group on UiO-66 to achieve the same gas adsorption as the one with 100% loading.

## 5. References

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- [2] Blanco, A.A.G., *Microporous and Mesoporous Materials* **224**, (2016) p. 323-331.