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Monolithic Composites of Metal-Organic Frameworks with Aerogels/Xerogels for Adsorbed Natural Gas Vehicles

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Three porous metal-organic frameworks (MOFs), $Cu_3(btc)_2$ (btc = benzene-1,3,5-tricarboxylic acid) named HKUST-1, $Cr_3F(H_2O)_2O(bdc)_3$ (bdc = benzene-1,4-dicarboxylic acid) named MIL-101 and $Zn_2(bdc)_2(dabco)$ (dabco= 1,4-diazabicyclo [2.2.2] octane) and their monolithic composites with silica aerogel were investigated for methane adsorption capacities to determine their potential use for natural gas storage in vehicles. The MOF composites were prepared to increase their methane uptake capacity on a volumetric basis by filling the interparticle void space with aerogel while keeping the volume of the MOF and composite constant. The MOFs were prepared using hydrothermal conditions, while their monolithic composites were synthesized by mixing the MOFs with aerogel solution made from methyltrimethoxysilane. X-ray diffraction (XRD) showed the MOFs were phase pure and highly crystallized and their composites maintained the original structure of the MOFs except in the case of $Zn_2(bdc)_2(dabco)$ composite as it reacted with aerogel precursor solution and transformed to a dense phase. Nitrogen isotherms at 77 K of all the samples except $Zn_2(bdc)_2(dabco)$ composite suggested that their shape is characteristic of Type I indicating their microporous nature. Methane adsorption was determined at room temperature up to 35 bars (See Figure 1). HKUST-1 and MIL-101 composites showed increases of 30.4 and 12.0 % when compared only with their MOFs, respectively in the methane adsorption capacities at room temperature and a pressure of 35 bars. In particular, methane adsorption capacity at room temperature using HKUST-1 aerogel composite was highly improved when compared to that of HKUST-1 by itself on a constant volume basis. The methane adsorption capacities increased by making monolithic MOF composites where the void space between the MOF particles was filled with hydrophobic and high surface area porous silica aerogels. Therefore, using monolithic aerogel MOF composites may be one way to increase natural gas storage in natural gas fueled vehicles. This could impact on the relevant industry by finding a solution to improve natural gas storage in vehicles. This project also impacted academia by making it possible to train scientists as human resources for industry. This research supported through ACS PRF was very helpful to my postdoc who participated in it to pursue a career in industry. By completing this research he could finish his postdoctoral training successfully and this experience definitely improved his ability to do research. He already succeeded in getting a job with industry. Through the research on natural gas adsorption on the aerogel-MOF composites, we could extend this knowledge and insights for future research, for example, in storing hydrogen gas. This funding helped me as the PI to conduct research actively and train a postdoc successfully. We will submit a manuscript for publication.

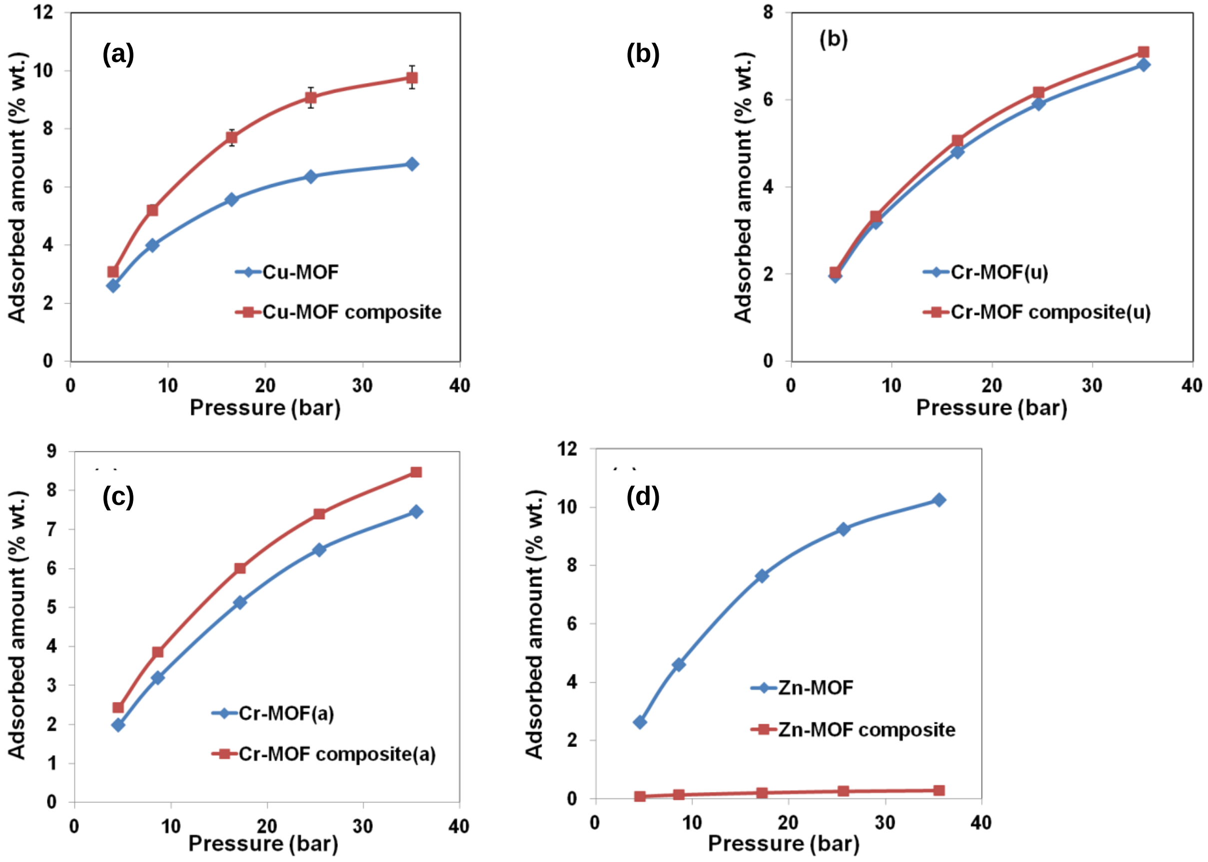

Figure 1. Methane adsorption up to 35 bars in MOFs and MOF composites. HKUST-1, MIL-101, and $Zn_2(bdc)_2(dabco)$ are referred to Cu-MOF, Cr-MOF, and Zn-MOF, respectively. Cr-MOF(u) was activated using ethanol at 100 ^{o}C for 20 hr to remove impurities from pores and designated to Cr-MOF(a).