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A novel bimetallic MIL-101(Cr, Mg) with high CO_2 adsorption capacity and CO_2/N_2 selectivity

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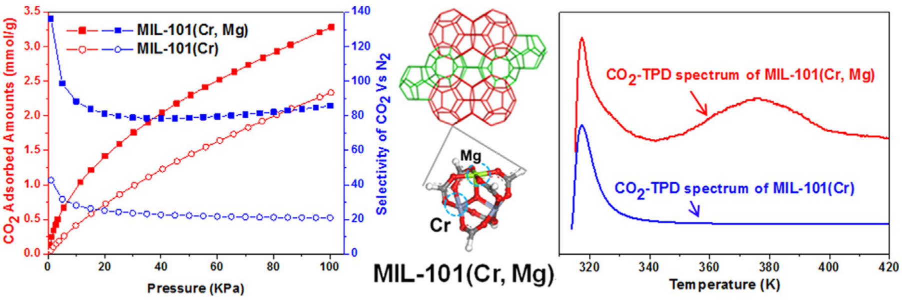
HIGHLIGHTS

- A novel bimetallic MIL-101(Cr, Mg) was successfully synthesized.
- New CO_2 adsorptive sites on MIL-101 (Cr, Mg) surfaces were formed due to Mg doping.
- The bimetallic MIL-101(Cr, Mg) exhibits higher CO_2 uptake than MIL-101(Cr).
- MIL-101(Cr, Mg) shows high CO_2/N_2 adsorption selectivity up to 86.
- Isosteric heat of CO_2 adsorption on MIL-101(Cr, Mg) is higher than that on MIL-101(Cr).

GRAPHICAL ABSTRACT



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ABSTRACT

A novel bimetallic MIL-101(Cr, Mg) was successfully synthesized for the first time by doping Mg during the solvothermal synthesis of MIL-101(Cr), and then characterized. The doped magnesium was homogeneously dispersed in the crystals of MIL-101(Cr, Mg). The magnesium ions had successfully coordinated with the carboxylic group in BDC through Mg–O. The synthesized MIL-101(Cr, Mg) remained excellent moisture-stability after exposed to humid air with 90% relative humidity for 30 days. Importantly, Mg doping not only made MIL-101(Cr, Mg) had higher surface area than MIL-101(Cr), but also created new and strong adsorptive sites for CO_2 confirmed by TPD experiments. As a result, CO_2 adsorption capacity of MIL-101(Cr, Mg) was significantly improved, and reached 3.28 mmol/g at 298 K and 1 bar, having an increase of 40% in comparison with MIL-101(Cr). More importantly, the CO_2/N_2 adsorption selectivity of MIL-101(Cr, Mg) was significantly enhanced up to 86 at 100 kPa, being ~4 times of that of MIL-101(Cr). The strategy of doping metal ions can be an effective way to improve the adsorption performance of MOFs.

1. Introduction

The mitigation of carbon dioxide is of particular importance as it has been considered as the major anthropogenic contributor to climate change globally (Sumida et al., 2011; Vlachos and Caratzoulas, 2010). Among the approaches to alleviating CO_2 emissions, CO_2 capture and separation showed great potential (Ho et al., 2008), where the design and development of advanced materials with characteristics of high sorption capacity, selectivity and thermodynamic stability for CO_2 capture play a key role.

As a new family of adsorbent materials, porous metal-organic frameworks (MOFs) have attracted significant attention worldwide (Kuppler et al., 2009; Liu et al., 2013; Venna and Carreon, 2015).

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The unique advantages of rich porosity and tunable surface functionalities of MOFs (Martínez et al., 2016; Tanabe and Cohen, 2011; Zhou et al., 2015a) made it promising in CO_2 adsorption-based capture and separations. Zhao et al. (2009) studied CO_2 uptake capacity on MOF-5 and reported that the CO_2 adsorption on MOF-5 was up to 2.10 mmol/g at 296 K and 1.0 bar. Britt et al. (2009) investigated the CO_2 adsorption on Mg-MOF-74, a framework with open Mg^{2+} sites and found its CO_2 adsorption capacity was of 35.2 wt% at 298 K and 1 bar. Millward and Yaghi (2005) studied the CO_2 adsorption on MOF-177 and reported its CO_2 uptake reached 33.5 mmol/g at 298 K and 35 bar. Furukawa et al. (2010) studied the CO_2 adsorption performance on MOF-200 and MOF-210, and reported that the CO_2 uptakes of these two MOFs were both up to about 71 wt% at 50 bar and 298 K. As one of the most stable MOFs, MIL-101(Cr) achieved a high CO_2 adsorption capacity of 23 mmol/g at 298 K and 30 bar (Zhang et al., 2011a).

To further enhance the CO_2 adsorption capacity and selectivity, the introduction of basic amine functional groups into MOFs via pre- or post-modification method were reported (Lin et al., 2012; Xian et al., 2015a', 2015b; Zhang et al., 2011b). Those amine groups can act as Lewis bases to bind CO_2 strongly and its nitrogen atoms contain lone pair of electrons, contributing to an enhanced affinity with carbon dioxide molecules (Vaidhyanathan et al., 2010). However, some of MOFs composites with loaded amine groups exhibit a greatly high adsorption heat (even up to ~100 kJ/mol (Hu et al., 2014)) due to the chemisorption, resulting in difficulty of desorption. Another approach by introducing carbon materials, such as graphene oxide, into MOFs was reported. The enhanced CO_2 adsorption capacity and selectivity were attributed to the increase in both BET surface area of MOFs and dispersive force of MOFs due to the incorporation of carbon materials. For example, Zhou et al. (2015a) and Huang et al. (2014) synthesized GrO@MIL-101(Cr) and GrO@Cu-BTC, respectively, and reported that their CO_2 adsorption capacities increased by 53.4% (at 298 K and 25 bar) and 26.2% (at 273 K and 1 bar) in comparison with pure MIL-101(Cr) and Cu-BTC.

Doping metal ions in MOFs during solvothermal crystallization can be another option for enhancing adsorption performance of MOFs, and the feasibility of this approach has been proven by some researchers. Jiao et al. (2015) reported MM-MOF-74 incorporated with three different metal ions (Mg^{2+}, Ni^{2+} and Co^{2+}) possessed tunable CO_2 adsorption properties. Botas et al. (2010) synthesized a Co doped MOF-5 adsorbent and reported that Co-MOF-5 presented a 17% increase in CO_2 uptake at 273 K and 10 bar compared to the parent MOF-5. Bae et al. (2011) prepared Li-doped MOF, and reported a 13% increase in CO_2 adsorption capacity but negligible increase (1% at 17 bar) in CH_4 uptake, resulting in an enhanced CO_2/CH_4 selectivity. Cao et al. (2014) reported that the HKUST-1 doped with moderate amount of K^+ showed 11% increase on CO_2 adsorption capacity at 298 K and 18 bar compared to HKUST-1. However, these metal-doped MOFs mentioned above were moisture unstable. Nevertheless, the previous work demonstrated that doping metal ions into MOFs may be an effective method for enhancing CO_2 adsorption capacity of MOFs and are worthy of further investigation. It is well-known that MIL-101 is one of the most porous materials to date. It has been considered as one of MOFs with super-high CO_2 adsorption capacity and excellent stability. It is a very promising adsorbent among the many MOFs that have been studied. However, to the best of our knowledge, doping metal ion in MIL-101(Cr) during solvothermal crystallization has not been reported yet.

Herein, Mg(II)-doped MIL-101(Cr) was synthesized for the first time to enhance its CO_2 adsorption capacity and CO_2/N_2 selectivity. The resulting MIL-101(Cr, Mg) was characterized by N_2 adsorption, X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and Fourier transform infrared spectroscopy (FT-IR). Isotherms of CO_2 and N_2 on MIL-101 (Cr, Mg) were measured, and ideal adsorbed solution theory (IAST) was applied to estimate the CO_2/N_2 adsorption selectivity. The isosteric heat of CO_2 adsorption over MIL-101(Cr, Mg) was also calculated. The change of CO_2 adsorption sites due to doped Mg(II) on MIL-101(Cr) was examined by TPD experiments. The mechanism for enhanced CO_2 adsorption and CO_2/N_2 selectivity over MIL-101(Cr, Mg) was further discussed and reported here.

2. Experimental

2.1. Materials

Terephthalic aicd (H_2BDC, 99%, A.R.), Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, 98%, A.R.) was purchased from Alfa Chemicals. Chromium nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, 99%, A.R.) was purchased from Tianjin Fuchen Chemicals Co. Ltd. (Tianjin, China). N,-N dimethylmethanamide (DMF, 99.5%) and ethanol (99.7%) were provided by Guangzhou Guanghua Sci-Tech Co. Ltd. Hydrofluoric acid (40%, corrosive, avoid contact with eyes and skin) was purchased from Guangzhou Chemical Reagent Factory.

2.2. Preparation of MIL-101(Cr, Mg)

MIL-101(Cr, Mg) was prepared by a doping strategy during solvothermal crystallization according to the following procedures. First, chromium nitrate(4.0 g, 10 mmol), terephthalic acid (1.64 g, 9.87 mmol), deionized water (48 mL) and HF solution(40%, 0.33 mL) were mixed in a Teflon autoclave reactor and stirred at 313 K for 10 min, and then magnesium nitrate hexahydrate was added into the mixture. Second, the autoclave was sealed in stainless steel vessels and set the temperature program: with 40 min raised from 40 °C to 220 °C, and incubated 8 h, followed by 3 h cooled to 160 °C, 3 h cooled to 90 °C, and 6 h cooled to 35 °C. Third, fine green powders were obtained as the major product, while a significant amount of recrystallized H_2BDC could be found. To acquire pure crystalline material with high porosity and surface area, a series of purifications were applied to remove the unreacted H_2BDC as well as other guest molecules in the product. Therefore, the resulting suspension was mixed with 25 mL DMF under vigorous stirring at 313 K for 30 min. Then, the slurry was filtered with G_1 funnel to remove unreacted precursors and the precipitate was further purified in ethanol (twice) and NH_4F solution (once, 30 mmol L^{-1}) respectively at 373 K for 12 h. After that, the slurry was washed with hot water for five times, and then filtered. Finally, the as-synthesized MIL-101(Cr, Mg) was dried at 373 K and then evacuated at 423 K for 12 h. During synthesis of MIL-101(Cr, Mg), the amounts of magnesium nitrate hexahydrate added as the reactants were separately 0.5, 1.0, 2.0 and 3.0 mmol in this work. Thus, the resulting MIL-101(Cr, Mg) adsorbents were correspondingly named as MIL-101(Cr, Mg)-1#, MIL-101(Cr, Mg)-2#, MIL-101(Cr, Mg)-3# and MIL-101(Cr, Mg)-4#. For comparison, conventional MIL-101(Cr) was prepared following the reported procedures (Liu et al., 2013).

2.3. Adsorbent characterizations

Nitrogen adsorption isotherms were measured at 77 K using a Micromeritics 3-Flex three stations fully functional surface area analyzer. BET and Langmuir surface area can be obtained by using the standard Brunauer–Emmett–Teller (BET) model and Langmuir model respectively in the pressure ranges of $0.05 < P/P_0 < 0.25$(based on the three consistency criteria) (Walton and Snurr, 2007). The samples were evacuated at 423 K for 8 h before measurements.