

Alkali metal cation doping of metal-organic framework for enhancing carbon dioxide adsorption capacity

Yan Cao^{a,b}, Yunxia Zhao^a, Fujiao Song^a, Qin Zhong^{a*}

a. School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, Jiangsu, China;

b. School of Environmental Science and Engineering, Yancheng Institute of Technology, Yancheng 224000, Jiangsu, China

[Manuscript received November 1, 2013; revised December 9, 2013]

Abstract

Metal-organic frameworks (MOFs) have attracted much attention as adsorbents for the separation of CO₂ from flue gas or natural gas. Here, a typical metal-organic framework HKUST-1 (also named Cu-BTC or MOF-199) was chemically reduced by doping it with alkali metals (Li, Na and K) and they were further used to investigate their CO₂ adsorption capacities. The structural information, surface chemistry and thermal behavior of the prepared adsorbent samples were characterized by X-ray powder diffraction (XRD), thermo-gravimetric analysis (TGA) and nitrogen adsorption-desorption isotherm analysis. The results showed that the CO₂ storage capacity of HKUST-1 doped with moderate quantities of Li⁺, Na⁺ and K⁺, individually, was greater than that of unmodified HKUST-1. The highest CO₂ adsorption uptake of 8.64 mmol/g was obtained with 1K-HKUST-1, and it was ca. 11% increase in adsorption capacity at 298 K and 18 bar as compared with HKUST-1. Moreover, adsorption tests showed that HKUST-1 and 1K-HKUST-1 displayed much higher adsorption capacities of CO₂ than those of N₂. Finally, the adsorption/desorption cycle experiment revealed that the adsorption performance of 1K-HKUST-1 was fairly stable, without obvious deterioration in the adsorption capacity of CO₂ after 10 cycles.

Key words

metal-organic framework; HKUST-1; carbon dioxide adsorption; alkali metals cation doping; adsorption-desorption cycles

1. Introduction

Since the industrial revolution the fossil fuel-dependent development has resulted in rapid increase of CO₂ concentration in the atmosphere, which has caused the global climate changes [1]. Carbon reduction has become a hot research area of experts from all walks of life over the world [2]. Nowadays, there are various approaches of CO₂ separation and storage, such as solvent absorption, chemical [3,4] and physical adsorption [5], membranes separation [6], cryogenic distillation [7], and so on. Compared with large-scale separation of CO₂ by liquid phase amine-based absorption, physisorption between solid adsorbents and CO₂ molecules is a reversible process that requires much less energy for desorption [8]. Thus, development of highly efficient solid sorbents for the capture of CO₂ has become more and more important.

Traditional solid adsorbents include activated carbons [9], zeolites [10], hydrotalcite [11], metal carbides [12,13], and amine-functioned porous materials [14]. Metal-organic frameworks (MOFs) as a novel type of porous crystal mate-

rials, have attracted extensive attention around the world, due to their extraordinary adsorption capacity of CO₂ [15]. MOFs are a type of novel crystal materials with periodic network structure, formed by self-assembly through covalent bond or inter-molecular forces between metal ions and organic ligands [16]. They have similar structures and properties to zeolites. Up to now, many MOF materials have been synthesized and tested for CO₂ adsorption. MOF-2 was the first MOF material which was used for studying CO₂ adsorption. The CO₂ adsorption capacity of MOF-2, as reported in Ref. [17], at 1 atm and 195 K was 2 mmol/g. Then, it was reported that MOF-177 exhibited a CO₂ adsorption capacity of 33.5 mmol/g at 298 K and 40 bar [15], which exceeded the CO₂ adsorption capacities of zeolites and activated carbons reported in literatures. Among the various MOFs reported, HKUST-1, firstly reported by Chui et al. [18], was assembled by the coordinate bond between Cu ions and tricarboxylate (H₃BTC) [18,19]. This MOF is easily synthesized by cheap primary compounds and is also commercially available now. HKUST-1 has been attracting much attention in both experimental research and theoretical simulation [20–23]. Millward et al. [21]

* Corresponding author. Tel: +86-25-84315517; Fax: +86-25-84315517; E-mail: zq304@mail.njust.edu.cn

evaluated the gravimetric CO₂ adsorption capacities on HKUST-1 in a range of 0–42 bar at ambient temperature, and they found an approximately fivefold higher CO₂ adsorption amount on HKUST-1 than that on MOF-177 under low pressure conditions. Xie et al. [22] tested the adsorption capacity of HKUST-1 and claimed that its adsorption capacity of CO₂ was about 69 mL/g at 295 K and low pressure. Moreover, they indicated that the adsorption capacity of CO₂ on HKUST-1 cannot be significantly influenced in the presence of main flue gas components such as SO₂, NO and H₂O. Yang et al. [23] performed a computational study on the adsorption separation of CO₂ from flue gases with a simulated mixture of CO₂/N₂/O₂ on HKUST-1. The computational results showed that HKUST-1 was a promising MOF material for the separation of CO₂ from flue gases, and gas compositions were important factors in optimizing the process of adsorption separation of gas mixtures. Taking the reported high thermal and structural stability of HKUST-1 and its excellent performance on CO₂ adsorption into account, HKUST-1 is considered as one of the promising adsorbents for CO₂ separation from flue gas [24,25].

In order to increase CO₂ uptake capacity together with the adsorption selectivity to CO₂ over other gases, various modifications have been applied to MOFs, such as cation exchange [26], formation of MOF-inorganic species composites (such as carbon nanotube [27], graphite oxide [28], and silica [29]) and the grafting of amine groups onto the coordinatively unsaturated MOF sites. Lan et al. [30] used the multi-scale simulation approach and indicated that Li was the best surface modifier of covalent organic frameworks (COFs) for CO₂ adsorption among a series of metals such as alkali metals (Li, Na, K), alkaline-earth metals (Be, Mg, Ca) and transition metals (Sc, Ti). Furthermore, their simulations showed that CO₂ uptakes of the lithium-doped COFs could be enhanced by four to eight times compared with the undoped COFs at 298 K and 1 bar. Xiang et al. [31] prepared the hybrid Li@CNT@[Cu₃(btc)₂], which was formed by the combination of Li doping and carbon nanotube incorporation. Toward this material CO₂ and CH₄ uptakes per effective specific surface area increased about 305% and 200%, respectively, compared with the unmodified MOF. Zhao et al. [32] synthesized the composites of HKUST-1 with aminated graphite oxide (MOF/GO-U). The MOF/GO-U3 composite exhibited an excellent CO₂ uptake capacity which is about 4.23 mmol/g at 298 K and 1 bar. Choi et al. [33] modified open metal coordination sites of Mg/DOBDC with ethylene diamine (ED) to introduce pendent amines into MOF micropores. This modified MOF, ED-Mg/DOBDC, had both improved CO₂ adsorption capacity at ultra-dilute CO₂ partial pressures and increased stability/regenerability.

To the best of our knowledge, few investigations have been focused on the influence of metal-doping on CO₂ capture, although this metal-doping strategy has been extensively studied in hydrogen storage which has been proven to be effective [34,35]. These motivate us to look into the effect of metals doping in MOFs on CO₂ capture. In this study, we evaluate the impact of doping of alkali metals (Li, Na and K)

in HKUST-1 on CO₂ capture. The adsorption properties of single-component CO₂ or N₂ were measured by static volumetric method on a homemade high-pressure adsorption apparatus. Moreover, the effect of water vapor on the structural stability was also evaluated. Additionally, the regenerability of the prepared adsorbents was examined via CO₂ cyclical adsorption/desorption experiment.

2. Experimental

2.1. Synthesis of HKUST-1

The synthesis and activation route of HKUST-1 was mainly followed the procedure reported by Chui et al. [18] with some amendments. Generally, 1,3,5-benzene tricarboxylic acid, H₃BTC (2 g, 9.5 mmol) was added into 60 mL DMF/ethanol (1 : 1 v/v) and stirred at room temperature for 10 min, then a solution of Cu(NO₃)₂·3H₂O (4.154 g, 17.1 mmol) in water (30 mL) was added into the mixture and stirred for 30 min. The resulting mixture was transferred into a 200 mL Teflon-lined autoclave for 10 h at a heating temperature of 373 K. After cooling slowly to ambient temperature, the blue powder was collected by repeated centrifugation and thorough washing with ethanol three times. After synthesis, the above crystalline materials were immersed inside chloroform solution for 2 d and then the solids were filtered. Finally, these materials were dried by heating at 373 K under vacuum overnight.

2.2. Synthesis of *n*M-HKUST-1

Lithium nitrate (LiNO₃), sodium nitrate (NaNO₃) or potassium Nitrate (KNO₃) was individually dissolved in DMF. The solution containing Li⁺, Na⁺ or K⁺, respectively, was then added into the solutions containing H₃BTC and Cu(NO₃)₂·3H₂O. The synthesis and activation of alkali metal cation doped HKUST-1 followed the same route of HKUST-1. The dark blue product was designated as *n*M-HKUST-1, where M represents the alkali metal cation (Li, Na and K) and *n* is related to the ratio of nitrate to pure HKUST-1.

2.3. Samples characterization

X-ray powder diffraction (XRD) patterns were taken on a XD-3 diffractometer (Beijing Purkinje General Instrument Co., Ltd, China) using Cu K_α radiation (λ = 0.15406 nm). The tube voltage was 35 kV, and the current was 20 mA. The XRD diffraction patterns were taken in 2θ range of 5°~80° at a scan speed of 8 °/min. Thermo-gravimetric analysis (TGA) was conducted with a SDTQ600 thermal analyzer (PerkinElmer Pyris Diamond, America). Analyses were done under a nitrogen atmosphere (30 mL/min flow rate) at a heating rate of 10 °C/min from room temperature to 600 °C. V-Sorbet 2008S surface area analyzer (Beijing Jinaipu General Instrument Co., Ltd, China) was used to measure the N₂ ad-

Download English Version:

<https://daneshyari.com/en/article/63979>

Download Persian Version:

<https://daneshyari.com/article/63979>

[Daneshyari.com](https://daneshyari.com)