



Enhancement effect of lithium-doping functionalization on methanol adsorption in copper-based metal-organic framework



Ying Wu^a, Defei Liu^a, Huiyong Chen^b, Yu Qian^a, Hongxia Xi^a, Qibin Xia^{a,*}

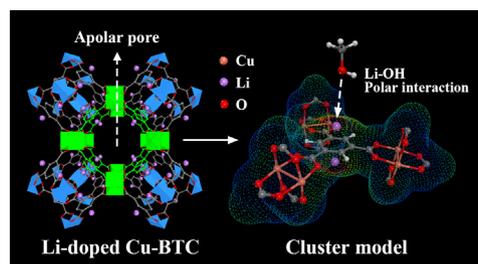
^a The School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong, People's Republic of China 510641

^b School of Chemical Engineering, Northwest University, Xi'an, Shaanxi, People's Republic of China 710069

HIGHLIGHTS

- Cu-BTC-Li has been theoretically constructed by ligand functionality of Cu-BTC.
- Li-doping effect on methanol adsorption over Cu-BTC is studied by GCMC-DFT method.
- Cu-BTC-Li shows higher capacity and more continuous sorption behavior than Cu-BTC.
- Electrostatic or dispersive interaction governs the adsorption at varied pressures.
- Li-doping improves adsorption by increasing electropositivity and dispersion.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 August 2014

Received in revised form

30 September 2014

Accepted 6 October 2014

Available online 16 October 2014

Keywords:

Adsorption

Li-doping functionalization

Cu-BTC

Methanol

GCMC

DFT

ABSTRACT

Grand canonical Monte Carlo (GCMC) simulations combined with density functional theory (DFT) calculations were performed to evaluate the functionality effect of Li-doping on methanol adsorption over copper-based metal-organic frameworks (MOFs). In this work, a new Li-doping structure, Cu-BTC-Li, was theoretically constructed by introducing Li above both sides of organic linkers in Cu-BTC. Compared to the original Cu-BTC, Cu-BTC-Li shows higher methanol capacity and more continuous adsorption behavior in the measured pressure range. It can be attributed to the new adsorption sites (Li-sites) created by Li atoms, which turn to be the first preferential adsorption sites instead of Cu-sites, as revealed by the more exothermic binding energies (BEs) on Li-site (-90.55 kJ/mol) than the latter (-45.14 kJ/mol). Li-doping also shows varied effects on methanol adsorption at different pressures. The electrostatic interaction between methanol and framework plays a predominant role (with contribution over 95%) in the adsorption at low pressures, and Li-doping enhances adsorption by increasing the electrostatic potential of the framework. Although the dispersive interactions govern the adsorption at high pressures, Li-doping contributes to the dispersion. The present Li-doped functionalization can be extended to design new MOFs with high performance of alcohol capture in the future.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Metal-organic frameworks (MOFs) are an emerging class of crystalline porous materials constructed by metal clusters and organic linkers. Possessing highly adjustable channels and large surface area, MOFs show great promises in numerous applications

* Corresponding author. Fax: +86 020 87113735.

E-mail address: qb Xia@scut.edu.cn (Q. Xia).

such as gas adsorption/separation (Jeong et al., 2012; Zhu et al., 2012), catalysis (Li et al., 2012), and drug delivery (Sun et al., 2012). Among MOFs, Cu-benzene tricarboxylic acid (Cu-BTC) (Chui et al., 1999) shows great potential for gas adsorption, owing to its dual merits of extra binding sites and structural stability that enable this material to have high performance of adsorption even in moist air (Martín-Calvo et al., 2011; Martín-Calvo et al., 2012; Murray et al., 2009).

To make a distinction of adsorption environment in the framework, three cage types were identified in Cu-BTC, as illustrated in Fig. 1. The small tetrahedral-shaped pockets (T1 cages) have a diameter of 5~7 Å (Chui et al., 1999; Getzschmann et al., 2010; Yang et al., 2003), formed by four BTC linkers and recognized as apolar in nature. Surrounded by these pockets, two types of large cages (L2 and L3 cages with diameters of 11~12 Å and 10~13.5 Å, respectively (Getzschmann et al., 2010; Yang et al., 2003)) are presented. L3 cages are more polar in nature, as they have open Cu atoms pointing inside the cages, whereas the L2 cages are relatively apolar as the lack of Cu atoms inward. The L3 cages are connected to eight T1 pockets through 3.5~4.6 Å (Chmelik et al., 2009; Yang et al., 2003) windows in diameter, while L2 cages communicate with the neighboring L3 cages by ~9 Å (Chmelik et al., 2009) windows but do not connect to the T1 cages.

In the last ten years, various studies have focused on the adsorption of small nonpolar molecules (e.g., H₂ (Krishna and van Baten, 2011; Moellmer et al., 2011), CH₄ (Chen et al., 2012; Getzschmann et al., 2010)) on Cu-BTC for hydrogen storage and methane purification. However, fewer researchers have investigated the adsorption of small alcohols (specifically, methanol), which are not only the notable examples of polar adsorbates on Cu-BTC, but also technologically urged by the demands toward volatile organic compound (VOC) captures (Kim and Ahn, 2012) and methanol economy (Olah, 2013).

In this respect, adequate attention should be paid to the study of alcohol adsorption, which aims in the study's consideration for clarifying the structure–property relationship and improving Cu-BTC with high performance of alcohol capture. Van Assche et al. (2013) reported the well-pronounced two-step adsorption isotherms of small alcohols (methanol and ethanol) on Cu-BTC, owing to the sequential adsorption behavior of the adsorbates. Jose et al. (Jose Gutierrez-Sevillano et al., 2013) suggested the blockage of polar cages by using ionic liquids that could enhance the alcohol adsorption over Cu-BTC in aqueous mixtures. On the basis of Jose's work, Gutierrez-Sevillano et al. (2013) shielded the metal sites of Cu-BTC with acetone and dimethyl ether to restrict water attack, and reported it could offer higher ethanol selectivity than the bare framework. These works reveal the significant role of coordinatively unsaturated metal sites (CUS) played in alcohol adsorption as they greatly interact with the polar molecules.

Nevertheless, previous studies also indicate a limitation of polar molecule (alcohol) adsorption in the apolar cages of Cu-BTC, owing to the lack of polarity in these cages that fail to offer strong interaction environment for the molecules. Thus, it is highly imperative to develop new materials with dense polar sites that allow them to have sufficient affinity with polar adsorbates.

Until now, several strategies, such as exposing metal sites (Banerjee et al., 2008; Debatin et al., 2010), decorating ligands with polar functional groups (Kim et al., 2013; Torrisi et al., 2013), and doping alkali metals (Wu et al., 2010) have been deployed to improve MOFs with high polarity. Among these strategies, ligand-based metal doping is a more generally applied approach to tailor framework polarity, because metal sites on linkers is not only capable of essentially increasing the local polarity of frameworks through the promotion of charge separation (Chu et al., 2012), but also more sterically accessible than the open sites in the corners (Getman et al., 2010). Han et al. (2011) theoretically investigated the functionalization of ZIFs with several alkali metals (Li, Na, and K), and suggested that Li was the best dopant for hydrogen capture, as Li can evoke the polarization of H₂ molecules (Vitulo et al., 2005). Lan et al. (2010) also reported the best performance of Li-doping for strengthening CO₂ adsorption on COFs among a series of metals. Motivated by these results, Xiang et al. (2011) experimentally incorporated Cu-BTC with Li ions and carbon nanotubes, and found the hybrid material to have significantly larger CO₂ uptakes (increased by 305%) than the bare MOF. In terms of alcohols adsorption, Oliveira et al. (2010) reported that the composite adsorbent of activated carbon doped with 21.3 wt % of LiCl possessed 86% higher adsorbed amount of methanol compared to the original sample. However, the underlying information about the effects of Li-doping to the polarity of Cu-BTC is still insufficient due to the limitation of experimental technology. As framework polarity plays a vital role for the adsorption of alcohols, it is highly desirable to investigate the impact of Li-doping on alcohol-framework interactions. Moreover, it is also worthwhile to clarify the interaction strengths as well as the orientations of alcohols toward the adsorption sites in the presence of Li atoms. To address such intents, experimental procedures should be compensated with computational techniques, which can provide molecular insights into the adsorption mechanism previously unclear through experiments.

In the present work, we theoretically constructed a new structure Cu-BTC-Li, by introducing additional Li atoms over both sides of the organic linkers of Cu-BTC. GCMC simulations were carried out to examine the adsorption isotherms and preferential adsorption sites on Cu-BTC-Li and Cu-BTC. The DFT calculations were subsequently adopted to investigate the electrostatic potential of the framework, the interaction energies, and the molecule orientations during the adsorption. Then, the influence

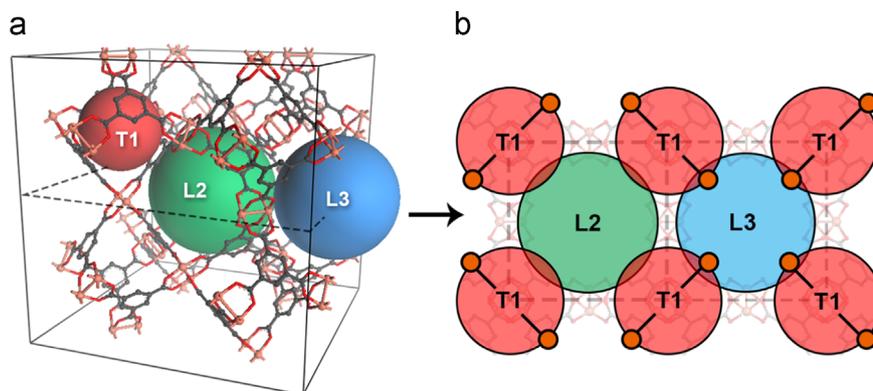


Fig. 1. The schematic of (a) 3-dimensional view and (b) top view of Cu-BTC model.

Download English Version:

<https://daneshyari.com/en/article/6590465>

Download Persian Version:

<https://daneshyari.com/article/6590465>

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