Microporous and Mesoporous Materials 266 (2018) 7–13

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Efficient thiophene capture with a hydrophobic Cu-BTC-(n)Br adsorbent in the presence of moisture

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ARTICLE INFO

Keywords:
Thiophene
Cu-BTC
Adsorption
Hydrophobicity

ABSTRACT

A novel hydrophobic adsorbent, Cu-BTC-(n)Br, was successfully synthesized by $Cu(NO_3)_2$ (metal ions source) and BTC-(n)Br (organic ligand) using a hydrothermal synthesis technology. Nitrogen adsorption-desorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR), and water contact angle are employed to characterize our obtained materials. Successful modification of these certain materials has been confirmed and the structural changes of them have been further explored. The efficient adsorption properties of as-prepared adsorbents for thiophene were evaluated by means of batch experiments. Compared with undressed Cu-BTC, Cu-BTC-(n)Br showed distinguished hydrophobicity and remarkable adsorption effectivity under aqueous circumstance. In addition, the adsorption process performance could be perfectly described by Langmuir adsorption model and pseudo-second-order equation. The hydrophobic Cu-BTC-(n)Br material might be a hopeful desulphurizer for real fuel in the presence of moisture.

1. Introduction

Thiophenic compounds (e.g. thiophene) capture has been a prevalent issue under research for promoting the development of oil refining industry along with environmental protection [1,2]. In fact, presence of water during real fuels production causes reduction of adsorption desulfurization efficiency cannot be ignored. Especially, water concentration in commercial fuels could be influenced by transport process, deployment and weather condition etc [3,4]. Metal–organic frameworks (MOFs) have attracted considerable attention in deep desulfurization field due to their flexible synthesis techniques in which the metal and/or organic ligand can be tailored to impart specific properties [4–6]. The thiophene capture process is mostly promoted by such a mechanism, the entering of thiophene into MOFs followed by the binding of MOFs with thiophene [2,4]. Though it may sound promising, the lethal attribute of MOFs-its hydrophilicity, makes this material almost futile of desulfurization under aqueous conditions, hindering its application in wider areas [4,7]. Li et al. [8] reported that H_2O is strongly adsorbed on Cu sites of Cu-BTC, which could strongly affect the desulfurization capacity. With 4 wt % of H_2O doping, Cu-BTC had such a dramatically reduced sulfur capacity that it almost became ineffective. The reduction of sulfur uptake capacity was not significant with further increasing with 18 wt % of H_2O doping amount. In our previously work [9,10], the sulfur breakthrough and saturation capacities of Zn/Cu–BTC adsorbents decreased sharply with the presence of dissolved water in the model fuels. Yang et al. [11] pointed out that the selective alkyl functionalization of organic ligands could create more open metal sites, improve their adsorption abilities of adsorbates, and reduce the effects casted on MOFs by water molecules all at once. As known from their work, 2-bromo-1,3,5-tri benzyl benzene was used as the matrix to synthesize the organic ligand 2-bromo-1,3,5-homobenzoic acid, and hydrophobic MOFs with bromine group was further synthesized to remove thiophene sulfur by adsorption. Thereby, designing and synthesizing MOFs that remain efficient of desulfurization in presence of water have drawn a lot of attention [12]. By changing the synthetic raw materials, or synthetic conditions, certain hydrophobic elements or functional groups can be introduced into the MOFs framework, thus reduce the combination of MOFs with water molecules [7,8,12].

Among the various MOFs, HKUST-1 (Cu-BTC), first reported by Chui et al. [13], is one of the most widely studied MOFs and it is suitable for application in deep adsorption desulfurization [8,14]. It is built from the paddle-wheel cluster consisting of Cu^{2+} ions coordinated to 1,3,5-benzenetricarboxylate organic linkers (BTC), forming an exceptionally rigid and highly porous network (Scheme S.I.1) with a high specific surface area. H_3BTC is a multidentate linker that allows for the formation of rigid frameworks through aggregation of metal ions into Cu-O-C clusters. Compared with other MOFs that do not possess open-

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https://doi.org/10.1016/j.micromeso.2018.02.032
Received 2 January 2018; Received in revised form 12 February 2018; Accepted 25 February 2018
Available online 02 March 2018
1387-1811/

metal sites, Cu-BTC has exhibited high adsorption selectivity for thiophenic compounds at room temperature [14]. However, the open-metal sites also have a strong affinity for water, which will decrease the S-capacity when present in moisture fuels [7,8,14].

Hence, in order to efficiently improve the uptake capacity and selectivity of the thiophene from moisture fuels, we report three isostructural copper-frameworks constructed from H_3BTC that has been functionalized with bromine (-Br) groups (Scheme S.I.2) for the first time in this work. Furthermore, the adsorption capacity of thiophene onto the novel hydrophobic MOFs was tested under aqueous conditions. Experimental results have convincingly proved that the introduction of certain amount of bromine atom into Cu-BTC could obviously ameliorate its thiophene capture ability under aqueous condition. Factors like water content and the number of introduced bromine atoms, that affect thiophene capture have been investigated into to figure out the better conditions for desulfurization. The equilibrium and kinetics parameters are studied to describe the rate and mechanism of the adsorption performance of obtained MOFs to determine the factors controlling the rate of adsorption, thereby finding out the possibility of using this MOFs material as an effective adsorbent for thiophene capture in the presence of moisture. In addition, distribution of thiophene sulfur between the liquid phase and the solid phase is also described by Langmuir and Freundlich isotherm models in this work. Langmuir isotherm refers to homogeneous adsorption, which each molecule possesses constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate) [15], with no transmigration of the adsorbate in the plane of the surface [16]. Freundlich isotherm [17] is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface [18].

2. Experimental

2.1. Preparation of BTC-(n)Br ligand

The preparation of organic ligand BTC-(n)Br was synthesized according to the references reports [19]. Briefly, for example, n(n = 1, 2 or 3)-bromo-1,3,5-trimethyl benzene (Sigma Aldrich, 98%, 20 g), and NaOH (Sigma Aldrich, 5 g) mixture was dissolved in 250 mL deionized water, and stirred magnetically for 10 min. Then 85 g $KMnO_4$ was added in the mixture solution mentioned above and continue to stir for 2 h. After that, the mixture solution was heated to 95 °C and stirred it for 3 d. The subsequent mixture was cooled down to room temperature and then filtrated. The filtrate was kept and be later acidized with concentrated hydrochloric acid. Next, extract the solution for several times using anhydrous ether to obtain organic phase, and then employ the low-pressure rotary evaporation to get the crude product (n)Br-BTC. In the end, wash the solids with petroleum ether for several times before rotary evaporation, and then the white-powdered, purified crude product organic ligand Br-H_2BTC, 2Br-HBTC and 3Br-BTC (5.09 g, 25%) were gotten. The reaction mechanism equation is shown on Scheme S.I.3.

2.2. Preparation of Cu-BTC-(n)Br

The sample, Cu-BTC-(n)Br, was synthesized using a slightly modified solvothermal method according to the literatures [13,14]. Briefly, cupric nitrate (0.21 g, 0.87 mmol) was mixed with Br-H_2BTC, 2Br-HBTC and 3Br-BTC (0.10 g, 0.48 mmol), and then grinded for 0.5 h with several drops of water. After that the mixture was transferred to a platform in a Teflon-lined stainless-steel autoclave (100 mL incapacity) with 10 mL DMF in the bottom. After reacted at 100 °C for 12 h, the obtained material was collected and washed with DMF three times, and then solvent exchanged with methyl alcohol, and dichloromethane for 24 h in sequence, respectively. The solid products (Cu-BTC-Br, Cu-BTC-2Br, and Cu-BTC-3Br) were washed with a water–ethanol mixture to remove any unreacted H_3BTC and dried overnight at 200 °C.

2.3. Samples characterization

The Brunauer − Emmett − Teller (BET) surface areas and pore size distributions of the adsorbents were determined by multipoint N_2 adsorption − desorption at liquid N_2 temperature (− 196 °C) on a physical adsorption instrument (Micromeritics, ASAP2020). Prior to analysis, all samples were subjected to a vacuum at 200 °C to ensure a clean surface. The specific surface areas were calculated using the standard Brunauer-Emmett-Teller (BET) method [20], which is the most widely used model for determining the specific surface area. The surface area of the samples was calculated from the nitrogen adsorption isotherms by assuming the area of a nitrogen molecule to be 0.162 nm^2. The micropore volumes was obtained from the *t*-plot method. The total pore volumes were estimated to be the liquid volumes of N_2 at a relative pressure of 0.99. The pore size distribution and average pore diameter were calculated using the nonlocal density functional theory (NLDFT) model [21]. X-ray powder diffraction patterns were recorded on a Philips PW 1710 diffractometer with automatic control. The patterns were obtained with monochromatic Cu Kα radiation with a scan rate of 2 °C·min^{-1}. Fourier transform infrared (IR) spectra were recorded on a Nicolet Nexus 470 spectrometer with KBr wafer. The contact angle of as-prepared MOFs was measured using a Dataphysics OCA20 contact angle system in ambient air at room temperature.

2.4. Batch experiments

Thiophene was dissolved in ALF (n-octane as the representative of aliphatic fuel) as the representatives of sulfur contaminants. In the process of H_2O pre-adsorption onto Cu-BTC and Cu-BTC-(n)Br, 1 g of vacuum-dried Cu-BTC and Cu-BTC-(n)Br samples were placed in a sealed container for 0.5 h with relative humidity of 33% controlled by a $MgCl_2$ saturated solution [8,22]. After that, the treated Cu-BTC and Cu-BTC-(n)Br samples were dried at 180 °C under vacuum and weighted every 0.5 h. For, example, the Cu-BTC and Cu-BTC-(n)Br samples with 5 wt % of preadsorbed H_2O were prepared when the sample weights reached 1.05 g, respectively, and then stored in a dried desiccator for use. Adsorption performances of Cu-BTC-Br, Cu-BTC-2Br, and Cu-BTC-3Br samples were studied by batch tests. 0.05 g of the adsorbent was equilibrated with 20 mL of ALF model fuel (The initial S-concentration is 760 ppm) in a polypropylene bottle on a thermostat rotary shaker. After equilibration, under appropriate external magnetic field, the magnetic samples and nonmagnetic samples were separated by centrifugation. The S-concentration was measured by a GC-2100 (Shanghai Shengyu Hengping Co., Ltd.) gas chromatograph (GC) equipped with a flame photometric detector (FPD). The S uptake (q_e), expressed as the amount of S removed per unit mass of the adsorbent was calculated according to following equation:

$$q_e = (C_o - C_e) \times (V/m) \quad (1)$$

where C_o and C_e are initial and equilibrium concentrations (mg·L^{-1}) respectively, m is the amount of the adsorbent (g) and V is the volume of the solution (L).

3. Result and discussion

3.1. Material characterization

3.1.1. N_2 adsorption-desorption isotherms

The BET surface area and total pore volume, which were calculated from nitrogen adsorption isotherms. The N_2 adsorption-desorption isotherms of Cu-BTC, Cu-BTC-Br, Cu-BTC-2Br, and Cu-BTC-3Br samples were presented on Fig. 1. According to the classification of IUPAC adsorption isotherms [23,24,25], the isotherm for Cu-BTC is of type I,