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Ultrahigh adsorption capacities of carbon tetrachloride on MIL-101 and MIL-101/graphene oxide composites

Yue Zheng, Fuchen Chu, Bing Zhang, Jun Yan, Yunlin Chen*

Institute of Applied Micro-Nano Materials, School of Science, Beijing Jiaotong University, Beijing 100044, China

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ABSTRACT

Hybrid composites of MIL-101(Cr) and graphene oxide (GrO) were prepared using a hydrothermal synthesis method. The synthesized materials were characterized using scanning electron microscopy, X-ray diffraction, FT-IR spectroscopy, thermal analysis and nitrogen adsorption. Results indicated that the specific area and pore volume of MIL-101/GrO-0.25 was much higher than pure MIL-101, and the adsorption capacities of carbon tetrachloride on the MIL-101 (Cr)/GrO was also higher than MIL-101. Moreover, the Langmuir-Freundlich (L-F) equation gave a well fit to the adsorption isotherm data of carbon tetrachloride. The result showed that the adsorption capacity of carbon tetrachloride on the MIL-101 at 303 K was 2044.4 mg/g, and the adsorbing amount on the MIL-101/GrO-0.25 was up to 2368.1 mg/g, which increased by 16% in comparison with the original MIL-101. The synthesized MIL-101/GrO composites exhibited a higher carbon tetrachloride uptake capacity than normal MIL-101 owing to the increasing of specific area, dispersion forces and defects on the crystal surface. Furthermore, the carbon tetrachloride uptakes of MIL-101 and MIL-101/GrO composites were well above those of conventional adsorbents, such as activated carbons and zeolites. It was demonstrated that the MIL-101 and MIL-101/GrO composite are promising adsorbents for application in the field of chlorinated volatile organic compounds (Cl-VOCs) adsorption.

1. Introduction

Volatile organic compounds (VOCs) are the main pollutants in the air, how to deal with it has become the focus of the society, many researchers are engaged in this field and have achieved a lot of effective results. Chlorinated volatile organic compounds (Cl-VOCs) are one subgroup of VOCs, which contain some chlorine in the compounds [1]. Most of Cl-VOCs have strong resistance to degradation [2], which are usually released from the production process of pesticide, adhesives and refrigerant, especially water disinfection process via chlorination [3]. Carbon tetrachloride is a principle member of Cl-VOCs, which usually been used as solvent in the chemical industry, such as soil, fat, rubber and resin etc. In addition, carbon tetrachloride is also been used as dry cleaning agent for fabric, metal detergent, insecticide and refrigerants [3]. However, it's worth noting that carbon tetrachloride exposure has serious hazard to human organs, such as kidney, liver, lung, it will also cause the damage on the central nervous system [4,5]. Among the existing methods of disposal Cl-VOCs, the adsorption technique has been intensively applied owing to its simplicity and safety, and the high-efficiency adsorbent is core of the adsorption technique [6–8]. Molecular sieves, activated carbons and zeolites have been generally used to adsorb Cl-VOCs, but it is still difficult to achieve higher adsorption capacity for carbon tetrachloride [9–11]. Hence, attempts to explore novel adsorbent with higher carbon tetrachloride uptakes will be valuable.

Recently, metal-organic frameworks (MOFs) which showed extra-high surface area, large pore volume, rich porosity and adjustable porous structure have attracted more attention [12,13]. Nevertheless, it was noticed that in spite of MOFs possess high adsorptive amounts, their low density of atoms, large amounts of void space and open frameworks cannot offer enough dispersive forces to bind the small molecule. It was demonstrated that the graphene oxide (GrO) was composited with MOFs could reduce these disadvantages [12,14,15]. Recently, the great interest has risen in graphene-based materials, the layered structure of graphene is extensible and controllable, during the oxidation process of it, more epoxy and hydroxyl groups may be introduced into the graphene layers, and more carboxylic groups may be located on the edges of GrO structure [14]. In other words, GrO can offer a favorable design platform for chemical modification, and this special structure of GrO makes MOFs-GrO materials have a potential to provide active sites for adsorption.

In the thousands of MOFs, MIL-101 was synthesized by Ferey and

* Corresponding author.
E-mail address: ylchen@bjtu.edu.cn (Y. Chen).

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his coworkers in 2005 [16], and then this porous material attracted intense research due to its high surface area and pore volume among the great family of porous materials [17–19]. In recent years, the researchers synthesized hybrid composites of MIL-101(Cr) and GrO to improve the adsorption amounts of MIL-101. For example, Ahmed et al. reported that the porosity of the composites increased remarkably when a small amount of GO (0.25%) was added in MIL-101 [15]. Sun et al. reported that the maximum n-hexane uptake on the MIL-101@GO composite was up to 1042.1 mg/g at 298 K, which increased 93% in comparison with pure MIL-101 [20]. Zhou et al. reported that the acetone adsorption capacity of GrO @MIL-101 was up to 20.10 mmol/g at 288 K, that having an increase of 44.4% than original MIL-101 [21]. However, the adsorption of carbon tetrachloride on the MIL-101 and MIL-101/GrO composites has not been reported yet, therefore, this problem is worth studying.

In this work, we prepared the MIL-101 and MIL-101/GrO materials, and the surface area and porosity of MIL-101/GrO composites are tunable via control the amount of GrO. The adsorption performance towards to carbon tetrachloride on MIL-101/GrO has been investigated for the first time. The resulting MIL-101/GrO-0.25 composite was demonstrated to improve carbon tetrachloride adsorption capacity. The effects of doping GrO on the adsorption performance of the composites were discussed.

2. Experimental

2.1. Materials

Hydrofluoric acid (HF, A.R.) was obtained from Beijing Chemical Works (Beijing, China). Chromium (III) nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$, 99%, A.R.) was purchased from Xilong Chemicals Co. Ltd. (Shantou, China). Terephthalic acid (H_2BDC, 99%) was purchased from Sinopharm Chemicals Reagent Co. Ltd. (Shanghai, China). Ammonium fluoride (NH_4F, 96%, A.R.) was purchased from Xilong Chemicals Co. Ltd. (Shantou, China). N,N-dimethylformamide (DMF, 99%, A.R.) was obtained from Tianjin Fuyu Fine Chemicals Co. Ltd. (Tianjin, China). Graphene Oxide (GrO) was purchased from Shanghai Ashine Technology Development Co. Ltd. (Changzhou, China). Carbon tetrachloride (CCl_4, 99%, A.R.) was obtained from Tianjin Fuyu Fine Chemicals Co. Ltd. (Tianjin, China).

2.2. Synthesis

The MIL-101 was synthesized via a hydrothermal method according to the literature procedure [16]. Firstly, $Cr(NO_3)_3 \cdot 9H_2O$ (2.4 g), H_2BDC (1 g) and HF (0.3 mL) were put into deionized water (30 mL), and the mixture heated at 493 K for 8 h. After cooled down to room temperature, the dark green solution was filtered to remove the unreacted H_2BDC, then the solution was centrifuged and dried to obtain the green powders which was the main product. To gain the pure crystalline material that have high porosity, a series of procedures for purification and activation were applied to the sample, which using N,N-dimethylformamide (50 mL), ethanol (50 mL) and NH_4F separately. After that, the product was washed with deionized water (90 mL) three times and dried. Finally, the MIL-101 sample was obtained.

The MIL-101/GrO composites were prepared by the similar method with MIL-101. The GrO content added in the precursor solution were separately 0.25, 0.5, 1 and 2 wt% of the initial material weight. The obtained materials are referred to as MIL-101/GrO-n where n = 0.25, 0.5, 1, and 2, representing the GrO amounts. We had tried to prepare the MIL-101/GrO composites with the GrO content of over than 2 wt%. However, when the mass fraction of GrO was higher than 2 wt%, the MIL-101/GrO composites cannot be prepared successfully and the samples may be physical or mechanical mixing.

2.3. Characterization

The morphology of MIL-101 and MIL-101/GrO composites was studied using a scanning electron microscopy, and it was performed on a FEI Quanta 650 field emission scanning electronic microscope at an accelerating voltage of 10 kV. In order to get the crystallization property, X-ray diffraction (XRD) patterns were obtained by BRUKER D8-Advance instrument with a scan speed of 4°/min. The FT-IR spectrum was measured using a SPECTRUM 400 system. The thermogravimetric analysis (TGA) was measured by SDT-Q600 heating from 303 K to 900 K in nitrogen atmosphere at a rate of 5 K/min, and derivative thermogravimetric (DTG) curves of samples were calculated from TGA datas. N_2 adsorption and desorption isotherms at 77 K were obtained by JW-BK122W instrument. The samples were outgassed at 378 K for 12 h before the measurement. The total pore volume was calculated at the relative pressure $P/P_0 = 0.99$. The mesopore volume was calculated by the Horvath-Kawazoe (HK) method, and the micropore volume pore size distribution was calculated by the Barret-Joyner-Halenda (BJH) method.

2.4. Carbon tetrachloride vapor adsorption experiments

The adsorption equilibrium experiments of carbon tetrachloride on the MIL-101 and MIL-101/GrO samples were measured by 3H-2000 PW Gravimetric Analyzer.

3. Results and discussion

3.1. Physical characteristics

Fig. 1 shows the SEM image of MIL-101, GrO and MIL-101/GrO Composites. Fig. 1 (a) indicates that the GrO had a layered structure, and Fig. 1 (b)-(e) shows the morphology of MIL-101 became more irregular with the increasing of GrO contents, and that sizes of composites were smaller than pure MIL-101. The octahedral morphology of MIL-101 sample is not obviously, which may owing to its crystal size is much smaller than other reports [22,23]. The size of crystallization can be determined by temperature and cooling rate of reaction. Fig. 1 (e) shows the most irregular crystal shape of MIL-101/GrO-2 sample. It might be excess GrO were composited with MIL-101 leading to the formation of MIL-101 crystal was prevented.

Fig. 2 shows the powder X-ray diffraction (XRD) patterns of all samples as well as pure GrO. The major peak of the GrO was located in 11°, which not observed in any MIL-101/GrO composites. In addition, the XRD peaks of MIL-101/GrO samples were almost the same as pure MIL-101, it also suggested that the synthesis of MIL-101 with a small amount of GrO was successfully. The main difference was that the intensity of MIL-101 and MIL-101/GrO materials, the maximum intensity was existed in MIL-101/GrO-0.25, as mentioned in previously reported [15]. On the contrary, the main peaks of MIL-101/GrO-2 composite were nearly disappeared, which means that the framework of MIL-101/GrO-2 may be collapsed. It indicated that the crystallinity of MIL-101 would increased owing to composite with the moderate content of GrO, but the distortion of the structure might occurred due to excess GrO was added into.

Fig. 3 gives the FT-IR spectra of the pure GrO and composites with different GrO contents. The vibrational peaks of GrO were reflected by carboxylic species, hydroxyl species and epoxy species (C=O, 1732 cm^{-1}; OH deformation, 1400 cm^{-1}; the C-OH stretching, 1229 cm^{-1}; C-O-C stretching, 1057 cm^{-1}; skeletal ring stretch, 1624 cm^{-1}) [24]. In addition, it was observed that the MIL-101 and all composites have similar spectrum. The carboxylate vibrations dominate the infrared spectra [25,26]. The original $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ modes of H_2BDC appeared at 1681 and 1285 cm^{-1} [27], and these peaks shifted to 1557 and 1403 cm^{-1} owing to the vibration frequency changing of carboxylic groups. This phenomena was probably because