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Materials Letters

journal homepage: [www.elsevier.com/locate/mlblue](http://www.elsevier.com/locate/mlblue)

## New challenge of microporous metal-organic frameworks for adsorption of hydrogen fluoride gas

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### ARTICLE INFO

#### Article history:

Received 24 November 2016

Received in revised form 16 March 2017

Accepted 21 March 2017

Available online xxxx

#### Keywords:

Porous materials

X-ray techniques

Metal-organic frameworks

HF adsorption

### ABSTRACT

To avoid the health threat and environmental pollution as well as to preserve the life of industrial equipment, it is very important and necessary to find an efficient method for detecting and eliminating HF gas. In the present work, four MOFs including Cu-BTC, ZIF-8, MIL-53(Al) and MIL-101(Cr) with various surface area, functionalities, and pore sizes were selected for their HF adsorption capacities studied under unique conditions. As comparison, commercial Al<sub>2</sub>O<sub>3</sub> powder and 13X zeolite were also investigated under the same conditions. It is resulted that the MOFs have higher HF uptakes than commercial Al<sub>2</sub>O<sub>3</sub> and 13X zeolite. MIL-53(Al) have a highest HF capacity, and the HF adsorption of MIL-101(Cr) can be regenerated up to 90%. To the best of our knowledge, this is the first work of studying the HF adsorption behaviors of MOFs, which provides a new perspective of MOFs in a new field of practical purify application.

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### 1. Introduction

Hydrogen fluoride (HF) is the principal source of fluorine for the synthesis of many important compounds including pharmaceuticals and polymers, thus is widely used in very large quantities in industries such as the semiconductor and petroleum industries [1]. As well known, HF is a very hazardous reagent because of its low boiling point and high toxicity [2,3]. However, in the practical production and employ processes, the excess of HF used is difficult to avoid the smuggling of small portion of HF gases completely. On the other hand, HF and/or other fluoride gases can generate in the application of fluoride compounds, such as SF<sub>6</sub> as electrical insulator [4,5], as well as coal combustion [6]. Moreover, HF gas in humidity will corrode the metal and insulation materials, and then break down the life of electric apparatus. Then again, the HF gas would yield in the running of pulse chemical laser based on the discharge of SF<sub>6</sub> and hydrocarbons, which would sharply decrease the performance of the laser [7]. Additionally, HF is the target analyte liberated in the hydrolysis of fluorinated G-type chemical warfare agents [8]. Therefore, to avoid the health threat and environmental pollution as well as to preserve the life of industrial equipment, it is very important and necessary to find an efficient method for detecting and eliminating HF gas [9].

Owing to the high toxicity, it is not easy to find a simple and safe way to remove HF gas. The simplest method is wet processing of the mixed gases. The mostly used absorption solution is soda water. This method is very effective and with low cost as well as the generation of cryolite which is very useful in electrolytic industry, hence was widely used before 1970s. However, the wet processing to remove HF gas has many limitations, including secondary pollution, large amount of water consumption etc., owing to the highly corrosive properties of hydrofluoric acid generating in the wet processing. Another approach to remove HF gas called dry defluorination technology is utilizing solid adsorbents, as an example of Al<sub>2</sub>O<sub>3</sub> which was also used early. Actually, because of the high chemical activity of HF gas, many kinds of solids can be used. However, the key problem is probably their limited HF gas uptake and poor purification efficiency of these solids. Microporous materials with high porosity and suitable pore sizes are usually used as solid adsorbents for gases [10]. The traditional microporous materials are crystalline zeolites and amorphous activated carbons, which are widely used in industry and our life.

Recently, a new family of crystalline microporous materials, called metal-organic frameworks (MOFs), has been widely investigated for the gas storage [11,12], catalysis [13,14], sensing [15,16] and nuclear wastes adsorption [17,18]. These kind of materials are composed of metals/metal clusters linked by organic ligands with coordination groups through coordination bonds [19]. The features of MOFs are the high surface area, tunable pore size and pore sur-

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face, which gives them more advantages in gas storage and separation than other microporous materials [20–22]. For example, some of them with unsaturated metal sites could give strong adsorptive interaction to gas molecules, such as  $H_2$ ,  $CH_4$ ,  $CO_2$ , etc [23,24]. In the present work, four stable MOFs including Cu-BTC, ZIF-8, MIL-53(Al) and MIL-101(Cr) with various surface area, functionalities, and pore sizes were selected for HF adsorption capacities studies under unique conditions. As comparison, commercial  $Al_2O_3$  powder and 13X zeolite were also investigated under the same conditions. To the best of our knowledge, this is the first work of studying the HF adsorption behaviors of MOFs.

## 2. Experimental

All reagents were commercially available and used as received without further purification. All the MOFs were synthesized and activated according to the reported processes [25–27], and the experimental details are summarized in the [Electronic Supporting Information \(ESI\)](#). Powder X-ray diffractions (PXRD) were carried out on Scintag X1 diffractometer with  $Cu K\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) at 40 kV, 35 mA. Gas sorption–desorption measurements were acquired on Autosorb-iQ2-MP-AG. The HF adsorption experiments were recorded by a homemade instrument illustrated in Scheme S1. The HF gas carried by the inactive  $N_2$  was purchased and used directly. *Caution!* The measurements had to be carried out at a ventilated place. Gas masks and latex gloves were needed. The experiments were carried out at 288 K. The volumetric ratio of HF in the mixed gas were measured in each time. The working capacity for HF adsorption of all the materials were obtained after calculation that is also in the [ESI](#).

## 3. Results and discussion

In this work, MOFs including Cu-BTC, ZIF-8, MIL-53(Al) and MIL-101(Cr) were selected for the HF adsorption for the first time. These MOFs are with various pore sizes, surface areas and functionalities (Fig. 1). Cu-BTC was firstly reported by Williams, I. D., also noted as HKUST-1 [28]. It was made of Cu paddle-wheel

dimers and the ligand benzene-1,3,5-tricarboxylic acid ( $H_3BTC$ ). The main channels of Cu-BTC is square that crossed in three dimensions of ca. 9  $\text{\AA}$  diameter. The BET surface area is ca. 1500  $m^2/g$  [29]. ZIF-8 is constructed by tetrahedral Zn ions and 2-methylimidazole (H-MeIM) with a SOD topology [26]. It is famous for its high stability and shows narrow size of pores (ca. 3.4  $\text{\AA}$ ). The BET surface area is ca. 1600  $m^2/g$ . MIL-53(Al) and MIL-101(Cr) are both synthesized by the hydrothermal reaction of metal nitrate and the ligand benzene-1,4-dicarboxylic acid ( $H_2BDC$ ) [30,31]. MIL-53 has flexible one-dimensional rhombic channels of ca. 8.5  $\text{\AA}$  diameter, and BET surface area of ca. 1100  $m^2/g$  [30]. MIL-101 was reported as one of early MOFs with mesopores. The structure of MIL-101 is constructed from super tetrahedrons connected each other with MTN zeolite topology. It have two kinds of cages with internal free diameters of ca. 29  $\text{\AA}$  and 34  $\text{\AA}$ , respectively. The pore windows is of ca. 12 and 14 respectively. The high BET surface area of MIL-101 is ca. 4200  $m^2/g$ , which was the highest among all the materials in 2009. Among these MOFs, Cu-BTC and MIL-101 would have open metal sites after activity. We also selected these MOFs because the relative low cost of ligands and high stabilities.

The powder X-ray diffraction (PXRD) performed on the as-synthesized MOFs is shown in Fig. 2. It can be seen that the peaks in PXRD patterns of all the MOFs are well agreed with the simulated patterns, which indicates that these materials were obtained successfully. We can also find that the peaks in PXRD patterns of as-synthesized MIL-101 is wide and weak, which could attribute to the low-quality crystallinity. To confirm their pore features, we also measured their  $N_2$  sorption isotherms at 77 K (Fig. S1). The BET surface area are 2125  $m^2/g$ , 1545  $m^2/g$ , 1185  $m^2/g$  and 2199  $m^2/g$  for Cu-BTC, ZIF-8, MIL-53(Al) and MIL-101(Cr), respectively. It can be seen that the surface area of MIL-101(Cr) is much lower than the reported, which may be caused by the low-quality crystallinity mentioned above and the  $H_2BDC$  ligands in the cages that cannot be easily removed [31]. However, the typical type IV sorption isotherms of MIL-101(Cr) also indicates the successful obtain of mesopores in MIL-101(Cr).

As mentioned above, the proportion of HF in the mixture gases was measured at the beginning of each adsorption testing. The cal-

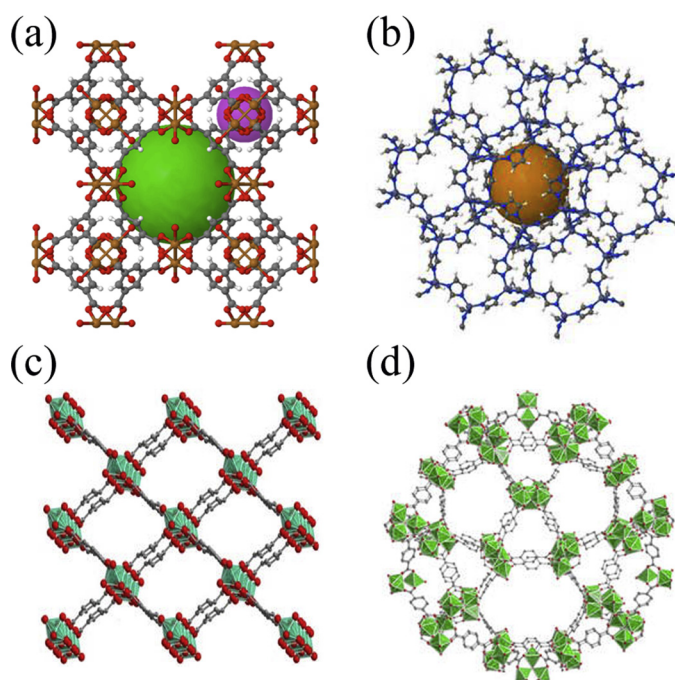


Fig. 1. The structures of: (a) Cu-BTC; (b) ZIF-8; (c) MIL-53(Al); (d) MIL-101(Cr).

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