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

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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_2O_3 powder and 13X zeolite were also investigated under the same conditions. It is resulted that the MOFs have higher HF uptakes than commercial Al_2O_3 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.

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_6 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_6 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_2O_3 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 Kα (λ = 1.5418 Å) 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 Å 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 Å). 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 Å 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 Å and 34 Å, 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-

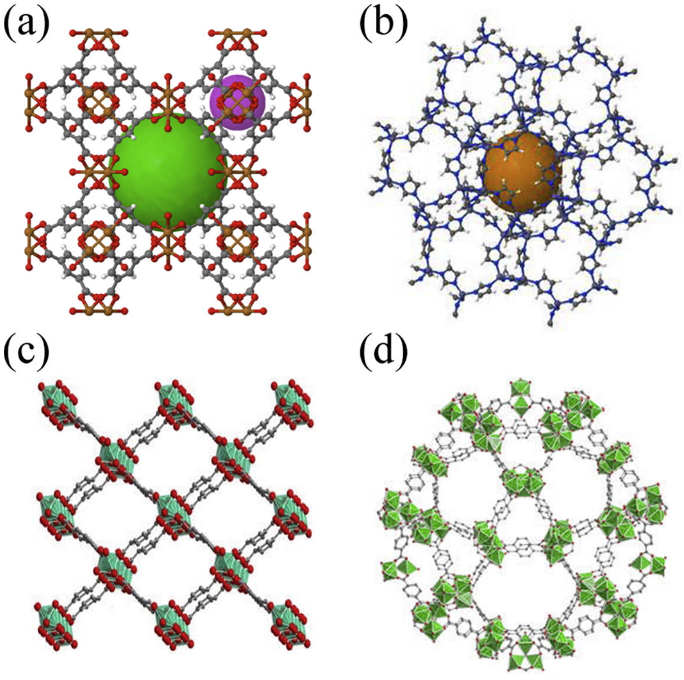

Fig. 1. The structures of: (a) Cu-BTC; (b) ZIF-8; (c) MIL-53(Al); (d) MIL-101(Cr).

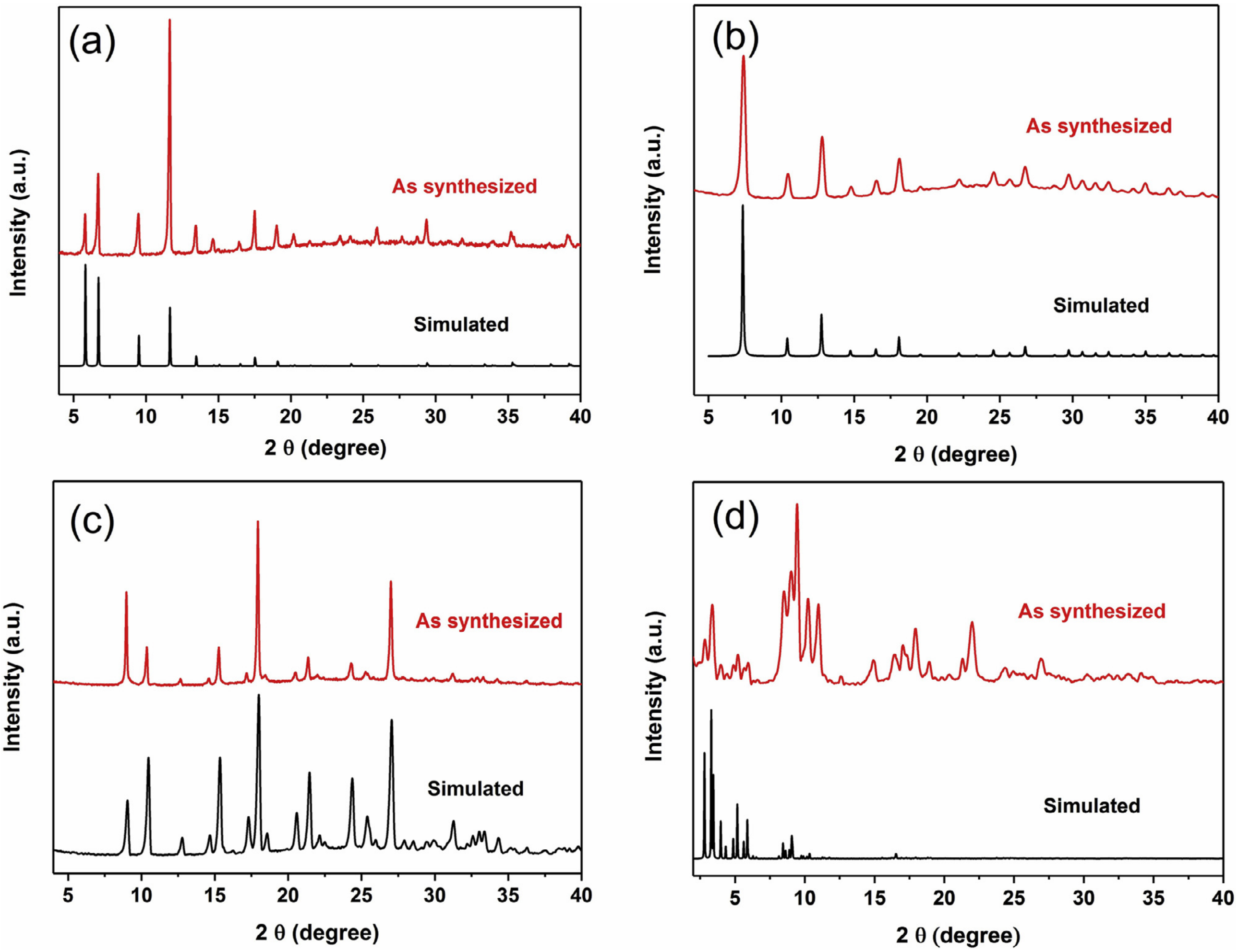

Fig. 2. The as-synthesized and simulated PXRD patterns of: (a) Cu-BTC; (b) ZIF-8; (c) MIL-53(Al); (d) MIL-101(Cr).

culation is based on Eq. (1) in ESI. The calculated result is list in Table S1. From the table, it is indicated that the molar ratio of HF (α_{HF}) is about 0.65, which is much higher that the made-up ratio (5%). It may be caused by lower density of HF gas than N_2. The high concentration of HF also raised the danger possibility in our measurement, and shortened the working life of the mixture gases of HF and N_2. It also can be seen that α_{HF} was very close in each time, indicating that the repeatability of our measurement.

The working adsorption of HF gas based on all the MOF-based materials as well as Al_2O_3 and 13X zeolite are list in Table 1. From the loading mass of the materials filling in the same tube, we can see that the highly porous MOFs and zeolite 13X are much lighter than Al_2O_3. The order of Al_2O_3 > 13X > Cu-BTC > ZIF-8 > MIL-53(Al) > MIL-101(Cr) would be the reverse order of their density. The working HF capacities of all the materials is 72.4 mg/g, 154.5 mg/g, 127.8 mg/g, 203.4 mg/g, 297.1 mg/g and 227.8 mg/g for Al_2O_3, 13X, Cu-BTC, ZIF-8, MIL-53(Al) and MIL-101(Cr), respectively. It can be seen that all the porous materials have much higher HF adsorption capacities than the conventional Al_2O_3. The order of working HF capacities is similar to that of surface areas. The contra-example is 13X and MIL-53, which is with higher capacities than Cu-BTC and MIL-101 relatively. It may be owing to the open framework of 13X and MIL-53. The highest capacity belongs to MIL-53. The HF adsorption is obtained as 14.86 mmol/g after calculation. It is worthy to know that the molar ration of captured HF to Al^{3+} of MIL-53 is about 3:1, which is close to stoichiometric ratio of aluminum trifluoride (AlF_3). This result suggests that chemical reactions may occur when exposing MIL-53 to HF gas.

The regeneration of materials is a key factor for practical applications, for saving the cost. All the materials after HF adsorption were treated at 100 °C for 12 h, aiming to active their capacities again. The HF adsorption results of materials after regeneration is

Table 1
HF adsorption by materials

Materials	Mass of Materials (g)	Gross of HF (mg)	HF absorbed by NaOH (mg)	HF adsorbed by materials (mg/g)
Al_2O_3	1.277	132.6	40.14	72.4
13X	0.7493	132.6	16.81	154.5
Cu-BTC	0.7080	132.6	42.09	127.8
ZIF-8	0.3313	132.6	65.20	203.4
MIL-53	0.3185	132.6	37.97	297.1
MIL-101	0.2913	122.6	56.24	227.8

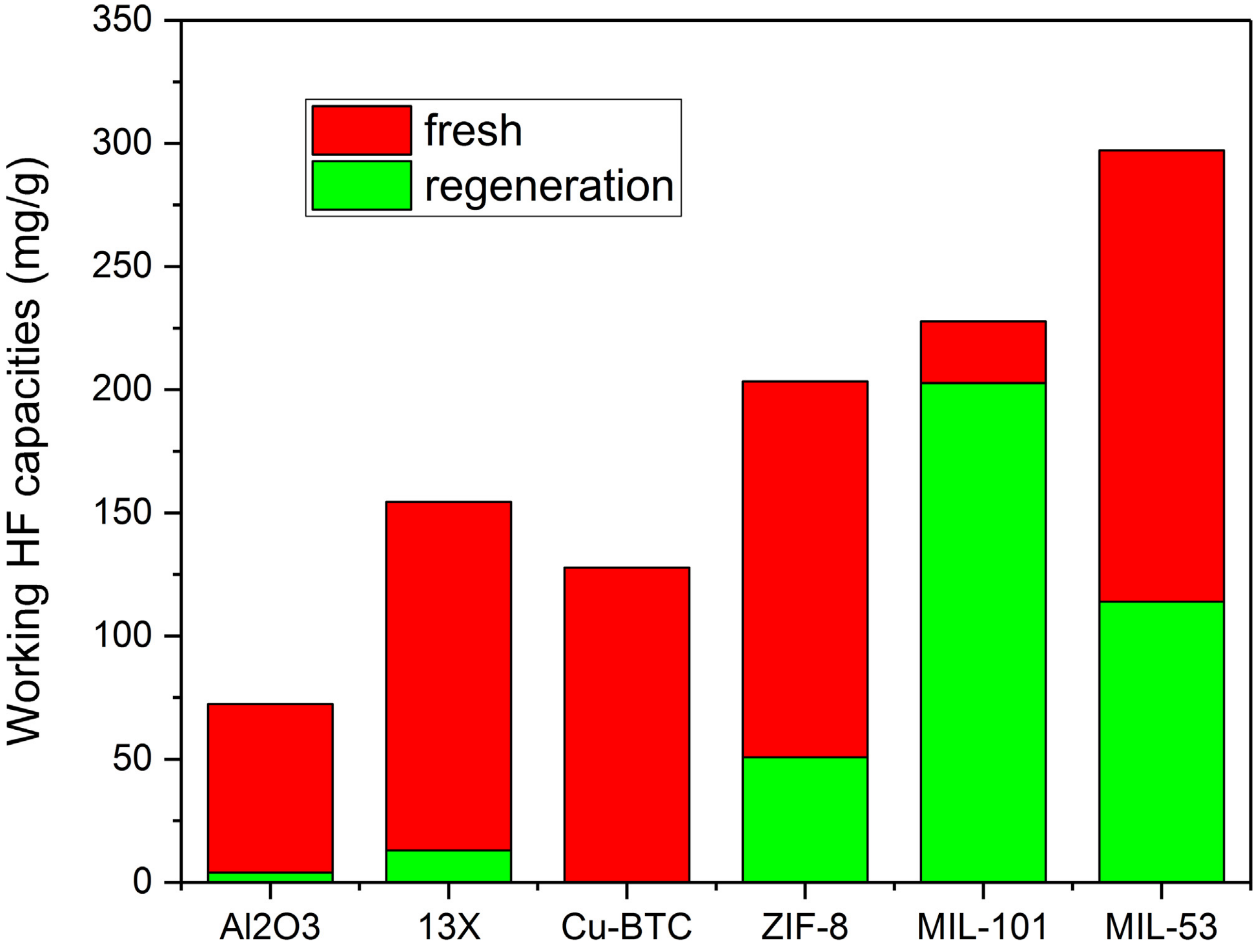

Fig. 3. Working HF capacity of Al_2O_3, zeolite 13X and four MOFs. Black columns: the fresh materials; red columns: the materials after regeneration.

shown in Fig. 3 and listed in Table S2. It is shown that Al_2O_3, 13X and Cu-BTC almost lost all the acyclic adsorption properties. It could also be seen that the Cu-BTC microcrystals were turned to blue powders obviously, indicating the highly decomposition of Cu-BTC. The HF adsorption capacities of ZIF-8 and MIL-53(Al) remained 25% and 38% respectively. The PXRD patterns of Cu-BTC, ZIF-8 and MIL-53(Al) after HF adsorption are with obviously decreased peak strength, indicating that their structural integrity was highly destroyed (Fig. S2). These results were coincident with the high chemical activity of HF, which was offensive for the coordination bonds in MOF's structures. Among all the materials in this study, only MIL-101(Cr) is some sort of regenerable. The remaining HF capacity of MIL-101(Cr) after regeneration is almost 90%, indicating the high stability of MIL-101(Cr) exposing to HF gas. However, the PXRD pattern of MIL-101(Cr) after HF adsorption is also with decreased peak strength, especially the disappearance of peaks before 4 degree of 2θ (Fig. S2). This result indicate that MIL-101(Cr) cannot be completely regenerated. The reason is supposed to be owing to the large pore structures and open metal sites in MIL-101(Cr) which have a buffer effect against acidic HF. Similar phenomenon was found in the adsorption of HCl gas by MIL-101 (Cr) [22].

4. Conclusions

In conclusion, 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. As comparison, commercial Al_2O_3 powder and 13X zeolite were also investigated under the same conditions. It is resulted that the MOFs have higher HF uptakes than commercial Al_2O_3 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%. This work provides a new perspective of MOFs in a new field of practical purify application.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.matlet.2017.03.111.

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