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Comparative Study of Hydrogen Sulfide Adsorption in the MIL-53(Al, Cr, Fe), MIL-47(V), MIL-100(Cr), and MIL-101(Cr) Metal−Organic Frameworks at Room Temperature

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The energetic transition from total petroleum consumption to consumption of reasonably clean and more energetic products[1] leads to a situation of main interest for natural gas and its applications. In this way, natural gas treatments are focused on removing naturally contained pollutants and added odorous compounds such as sulfur compounds. The gas industry has developed absorption techniques to remove the main part of these sulfur compounds with amine treatments,[2a] but porous solids are also envisaged in order to lower the final sulfur content and then reach the environmental requirements.[2b] Because of chemisorption effects and/or highly energetic regeneration costs that occur for most porous solids in the presence of H_2S, the number of suitable adsorbents for such applications is strongly reduced.[3] Metal−Organic Frameworks (MOFs) are crystallized hybrid porous solids built from inorganic subunits (clusters, chains, or layers) connected through organic linkers such as carboxylates or phosphonates.[4] They exhibit a huge variety of structures, sometimes with very large pores and high surface areas, leading to excellent adsorption properties for noncorrosive gases (H_2, CH_4, CO_2, etc.).[5] On the other hand, the study of their sorption properties relative to sulfur compounds has been limited to thiophene derivatives,[6] and their stability in the presence of reactive species (as simple as H_2O) is in many cases limited.[7] This paper presents the first experimental study of hydrogen sulfide adsorption in some porous MOFs, including their H_2S adsorption isotherms and an analysis of their regeneration, and shows that selected MOFs can be stable and easily regenerable toward H_2S sorption, representing a first step toward their use for the purification of natural gas.

Experiments were performed on two types of MOFs, exhibiting either small or large pores (Figure 1). The first series included the rigid ($M = V^{IV}$, later denoted MIL-47, where MIL stands for Matériaux Institut Lavoisier) and flexible (M^{III} = Al, Cr, Fe, later denoted MIL-53) solids formulated as $M(X)\{O_2C-C_6H_4-CO_2\}$ ($X = O$ for $M = V^{IV}$, OH for $M = Al^{III}$, Cr^{III}, Fe^{III}).[8a−d,g] Their three-dimensional frameworks are built up from corner-sharing chains of $M^{IV}O_6$ or $M^{III}O_4(OH)_2$ octahedra connected through terephthalate moieties. This delimits a one-dimensional diamond-shaped pore system with a BET surface area of $\sim$1000 $m^2\ g^{-1}$ (M = Al, Cr, V).[8e−g] The second class of MOFs considered in this study included the rigid chromium-based solids $Cr_3F(H_2O)_2O\{C_6H_3(CO_2)_3\}_2$ (denoted MIL-100) and $Cr_3F(H_2O)_2O\{O_2C-C_6H_4-CO_2\}_3$ (MIL-101). These two solids are made of trimers of chromium octahedra linked with trimesate and terephthalate, respectively, forming supertetrahedral motifs that further assemble to produce crystallized mesoporous hybrid solids with large BET surface areas exceeding 2000 $m^2\ g^{-1}$.[8e,f] MIL-47(V), MIL-53(Al, Cr, Fe), MIL-100(Cr), and MIL-101(Cr) solids were synthesized and activated as reported previously, except for MIL100 and MIL-101, where the as-synthesized solids were used.[8]

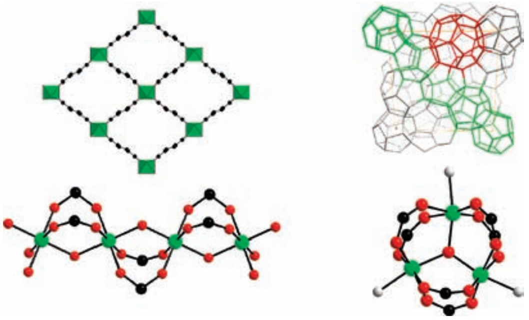

Figure 1. (top left) Structure of the MIL-47(V) and MIL-53(Al, Cr, Fe) solids. (top right) View of the structure of MIL-100(Cr) and MIL-101(Cr). The corresponding inorganic subunits are shown below each structure. Metal, oxygen, and carbon atoms are shown in green, red, and black, respectively, while terminal water molecules and fluorine are shown in gray.

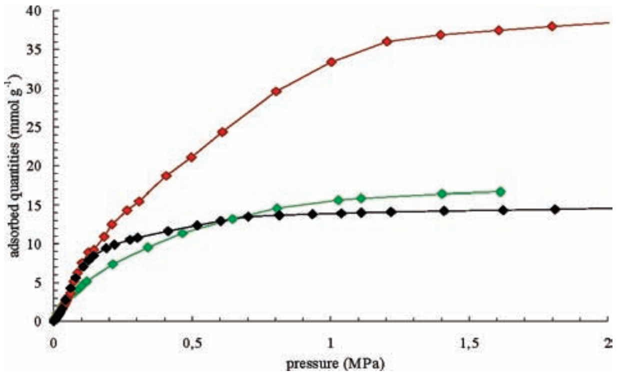

Figure 2. Excess adsorbed quantities of hydrogen sulfide on MIL-47(V) (black), MIL-100(Cr) (green), and MIL-101(Cr) (red) at 303.1 K for pressures up to 2.0 MPa.

Adsorption isotherm measurements were performed with a built-in-house apparatus based on a high-pressure magnetic suspension balance marketed by Rubotherm (see the Supporting Information). Hydrogen sulfide and methane adsorption capacities were measured at 303.1 K as a function of the pressure.

Solid samples (0.30−0.50 g) were initially outgassed under secondary vacuum (10^{-5} mbar) at 393.1 K for MIL-53(Cr, Al, Fe), MIL-100(Cr), and MIL-101(Cr) and 473.1 K for MIL-47(V).

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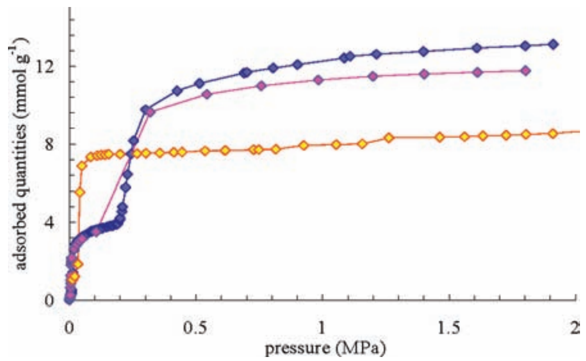

Figure 3. Excess adsorbed quantities of hydrogen sulfide on MIL-53(Cr) (pink), MIL-53(Al) (blue), and MIL-53(Fe) (yellow) at 303.1 K at pressures up to 2.0 MPa.

Figures 2 and 3 present the H_2S adsorption isotherms of the MIL-53(Al, Fe, Cr), MIL-47(V), MIL-100(Cr), and MIL-101(Cr) solids at 303.1 K for pressures up to 2.0 MPa. For a better understanding of the different behaviors at low pressure, an enlargement is shown in Figure 4 for results at pressures up to 50 kPa.

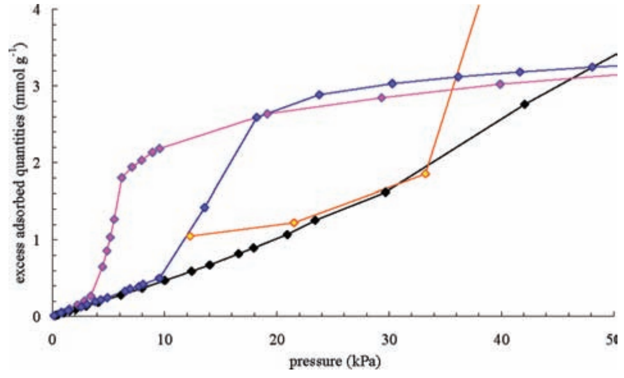

Figure 4. Excess adsorbed quantities of hydrogen sulfide on MIL-47(V) (black), MIL-53(Cr) (pink), MIL-53(Al) (blue), and MIL-53(Fe) (yellow) at 303.1 K for pressures up to 50 kPa.

As expected, the rigid and large-pore MIL-100 and MIL-101 solids exhibit H_2S adsorption isotherms with a monotypic type-I shape. The corresponding Henry constants are 72.9 and 61.3 mmol g^{-1} MPa^{-1}, respectively, while the maximum adsorbed quantities at 2 MPa are huge: 16.7 and 38.4 mmol g^{-1}, respectively.

In the case of the smaller-pore-size MIL-47(V) and MIL-53(Al, Fe, Cr) solids, the situation depends on the rigidity/flexibility of the network. Whereas MIL-47(V) presents a monotonic type-I-shaped isotherm with a Henry constant of 47.0 mmol g^{-1} MPa^{-1} and a maximum adsorption capacity of 14.6 mmol g^{-1}, the MIL-53 phases are very different, with two-step adsorption isotherms. To check the reproducibility of these results, the experiments were repeated twice with no difference in the isotherms. After a quasi-Henry zone at very low pressures, the MIL-53(Cr, Al, Fe) isotherms present first steps beginning at 4.5, 9.0, and 9.0 kPa for the Cr, Al, and Fe solids, respectively. The first step adsorbed reaches saturation at 3.02, 3.24, and 1.18 mmol g^{-1}, respectively, for the three solids. The second steps begin at 118, 210, and 33 kPa, respectively, and the corresponding maximum adsorbed quantities are 13.12, 11.77, and 8.53 mmol g^{-1} at high pressure (1.6 MPa). Such unusual behavior has been observed previously for MIL-53(Cr, Al) with polar molecules such as water and carbon dioxide and attributed to a breathing of the porous solids.[8b,c,9] If the outgassed MIL-53(Al, Cr) solids exhibit an open structure, a closure of the pores occurs at low gas or vapor loading as a consequence of either strong hydrogen bonds (H_2O) or donor−acceptor interactions (CO_2) between the guest molecules and the inorganic chains. At higher loading, a total opening of the pores occurs for CO_2, in agreement with weaker host−guest interactions, while no similar high-pressure experiment using water vapor has been performed to date. In the case of H_2S, we estimate that the polar H_2S molecules might strongly interact with the OH groups of the inorganic chains, leading to a closure of the pores at low loading. The reopening at higher pressure would correspond again to a breaking of the strong H_2S−OH interactions and a total filling of the pores with weak host−guest interactions. A comparison of the behaviors of MIL-53 and MIL-47 corroborates this assumption. The latter, which exhibits the same structure but no OH group, presents a type-I isotherm upon H_2S sorption, characteristic of a rigid microporous solid. Moreover, the capacities of MIL-47 and MIL-53(Al, Cr) at high pressure are similar, which seems to indicate that the pores in MIL-53 reopen at high pressure. This hypothesis will be confirmed soon by in situ IR experiments as well as computer modeling calculations.

In a second step, to check both whether the MIL solids were damaged upon adsorption of H_2S and whether physisorption or chemisorption occurred, CH_4 adsorption experiments were performed at room temperature both before and after the H_2S experiments (Figures 5 and 6) for all of the solids except MIL-53(Fe), since this one was destroyed by the H_2S treatment, as evidenced by the formation of a black powder (iron sulfur) and the crystallization of terephthalic acid at the surface of the adsorption cell. The CH_4 isotherms are of type I (no adsorption step), in agreement with previous results.[5f,10]

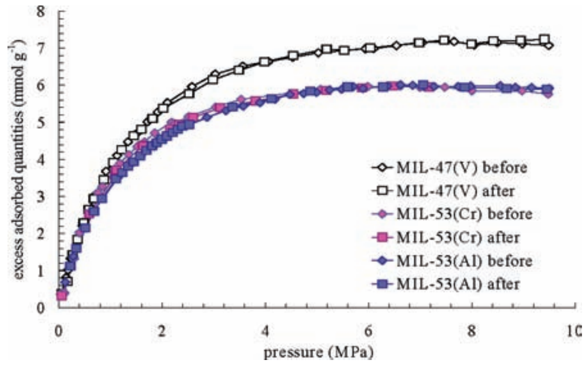

Figure 5. Excess adsorbed quantities of methane on MIL-47(V), MIL-53(Cr), and MIL-53(Al) before and after hydrogen sulfide treatment at 303.1 K with regeneration under primary vacuum (10^{-3} mbar).

A series of tests was performed in order to determine the best regeneration temperature for each MIL-*n* solid. It was found that MIL-47(V) and all of the MIL-53's except MIL-53(Fe) recover their initial weight after vacuum treatment for 8 h at 393.1 K. MIL-47(V) and MIL-53(Al, Cr) present exactly the same methane adsorption capacities before and after the H_2S treatment. Hydrogen sulfide desorption measurements performed on MIL-53(Al) at 303.1 K exhibit a desorption curve with the same curve shape as the adsorption one, with a shift of the steps to lower pressures (see the Supporting Information); this hysteresis curve was observed previously during the desorption of CO_2 with an even greater shift.[9a] These desorption measurements testify that only physisorption phenomena occur during H_2S adsorption on the MIL-53(Cr, Al) materials, allowing complete regeneration of the material.

Regeneration tests performed on MIL-101(Cr), which was outgassed at 423.1 K, showed a tiny difference. A BET surface

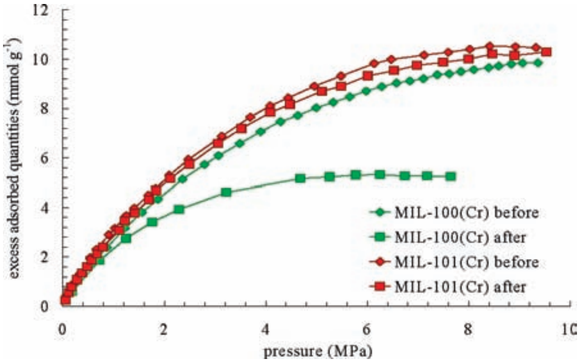

Figure 6. Excess adsorbed quantities of methane on MIL-100(Cr) and MIL-101(Cr) before and after hydrogen sulfide treatment at 303.1 K with regeneration under primary vacuum (10^{-3} mbar).

area variation before and after H_2S treatment was measured: it decreased from 2600(40) m^2 g^{-1} to 2550(40) m^2 g^{-1} upon sulfuration, presenting a S/Cr ratio of 0.07. For MIL-100(Cr), the first test (outgassing temperature 423.1 K) showed a significant decrease in CH_4 adsorption capacity. Increasing the outgassing temperature to 473.1 K did not further affect the adsorption capacity. BET surface area measurements exhibited a decrease from 1900(50) m^2 g^{-1} to 1650(50) m^2 g^{-1} before and after hydrogen sulfide treatment. Sulfuration of the sample with a S/Cr ratio similar to that of MIL-101(Cr) was observed.

The adsorption of H_2S in the large-pore MIL-100 and MIL-101 solids thus appears to be partially irreversible, either because of a partial destruction of the framework or because of strong interactions between the framework and the H_2S molecules, leading to incomplete evacuation upon outgassing under our experimental conditions. On the other hand, the small-pore MIL-47(V) and MIL-53(Al, Cr) exhibit perfectly reversible one- or two-step adsorption behavior under H_2S pressure, while the Fe analogue is destroyed under the same conditions. This study thus makes clear that judicious choices of structure type and metal lead to MOFs that are stable and easily regenerable upon H_2S sorption, representing a first step toward their use for the purification of gas containing sulfur impurities. Preliminary simulations performed on the non-flexible MIL-47(V) suggest a high selectivity of ~30 for H_2S versus CH_4 at 1.0 MPa (see the Supporting Information). Moreover, the steps observed during H_2S adsorption and desorption, which were not observed for methane adsorption, could be of most interest for pressure swing adsorption (PSA) processes, increasing the dynamic capacity of such processes, i.e., the difference between the adsorption capacities during the production (at high adsorption pressure) and regeneration (at low pressure) steps.

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Supporting Information Available: Details of adsorption isotherm measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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