Tuning the Channel Size and Structure Flexibility of Metal−Organic Frameworks for the Selective Adsorption of Noble Gases

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S Supporting Information

ABSTRACT: Two ultramicroporous metal−organic frameworks, $Zn(ox)_{0.5}(trz)$ and $Zn(ox)_{0.5}(atrz)$ (ox = oxalate, trz = triazolate, and atrz = 3-aminotriazolate), have been synthesized and tested for the adsorptive separation of Xe and Kr. We demonstrate that the Xe/Kr adsorption selectivity relates to the pore size as well as the structure flexibility of the adsorbents.

The separation of molecules with similar physical and chemical properties such as ethylene/acetylene, hexane isomers, and Xe/Kr into pure individual components represents a challenging yet important process in industry.[1] The current separation of these mixtures is largely accomplished by distillations, which commonly involve complicated column systems with high energy consumption.[2] Adsorptive separation by porous solids has been proposed as an alternative technology to distillations, with lower energy input and suppressed carbon dioxide emission. The implementation of an adsorptive separation technique primarily relies on the development of optimal adsorbent materials. Traditional adsorbents including zeolites, porous metal oxides, and activated carbons have been extensively investigated for the above-mentioned challenging separations. Compared to these prototype porous materials, the newly emerged metal−organic frameworks (MOFs) bear particular advantages for the challenging molecular separations in light of their highly tunable pore structure (pore size and pore shape) and surface functionality. MOFs have demonstrated exceptional performance in separating paraffin/olefin, alkane isomers, etc., which give them great potential for industrial implementation.[3−8]

Among the aforementioned gas mixtures, Xe/Kr has drawn relatively less attention mainly because of their low abundance. However, the high value and wide use of Xe and Kr gases pose particular importance for their separation. Binary mixtures of Xe and Kr exist as byproducts in the process of air separation, with a rough composition of 20% Xe and 80% Kr by volume, which is subject to further separation into pure components.[9] The adsorptive separation of Xe and Kr has been tested with

various porous solids including zeolites and carbons, but they generally suffer from relatively low selectivity.[10,11] The separation is challenging because Xe and Kr are atomic gases with similar molecular size (kinetic diameter: 4.0 Å for Xe and 3.7 Å for Kr). In the past few years, MOFs have shown great promise in separating Xe and Kr because of their tunable pore aperture as well as pore surface functionality (e.g., open metal sites).[12−14] However, improving their Xe/Kr adsorption selectivity remains a critical aspect of research that may be achieved by optimizing the MOF porosity based on material design strategies. Herein, we report the selective adsorption of Xe from Xe/Kr mixtures by tuning the pore size and structure flexibility of two ultramicroporous MOFs, $Zn(ox)_{0.5}(trz)$ and $Zn(ox)_{0.5}(atrz)$. The former show high adsorption selectivity, as confirmed experimentally by column breakthrough measurements.

$Zn(ox)_{0.5}(trz)$ (compound **1**) and $Zn(ox)_{0.5}(atrz)$ (compound **2**) were prepared through solvothermal reactions following reported procedures.[15] These two compounds were selected for evaluation of the adsorptive separation of Xe and Kr because of their suitable pore sizes as well as their high water/thermal stability. In both structures, each Zn^{2+} cation is five-coordinated to three different trz or atrz linkers through Zn−N bonds and to two O atoms from an ox linker. The two-dimensional Zn(trz) and Zn(atrz) sheets are pillared by oxalates, forming a three-dimensional (3D) network containing one-dimensional (1D) channels with channel diameters of 4.02 and 2.12 Å (O−O distance, excluding the van der Waals radius; Figure S5) for compounds **1** and **2**, respectively (Figure 1). The notably contracted channels in compound **2** are a result of the introduction of amino functional groups, leading to rotation of the oxalate pillars. Both compounds show exceptional stability upon exposure to moisture or liquid water.[15]

It has been predicted by a high-throughput computational modeling study that MOFs with 1D channels slightly larger than the atomic size of Xe are optimal for the separation of Xe
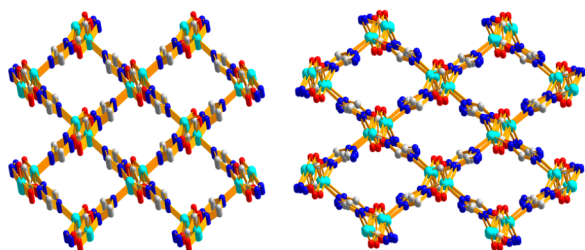
Figure 1. Perspective views of the 3D structures of compounds **1** (left) and **2** (right). Color code: Zn, cyan; O, red; N, blue; C, gray. H atoms are omitted for clarity.

and Kr.[16] Thus, compound **1** was first tested for the adsorption of Xe and Kr. Adsorption−desorption isotherms of Xe and Kr on compound **1** at 278, 288, and 298 K display type I profiles with no or negligible hysteresis, indicating their physisorption nature (Figure 2). Different from Kr isotherms, which are
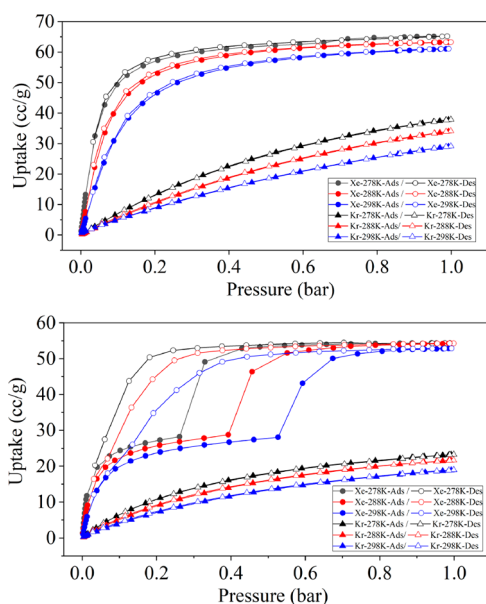

Figure 2. Adsorption−desorption isotherms of Xe and Kr on compounds **1** (top) and **2** (bottom) at different temperatures.

almost linear in the pressure range studied, the adsorption isotherms are much steeper for Xe at a relatively low-pressure region, suggesting stronger adsorbate−adsorbent interaction. The calculated isosteric heat of adsorption (Q_{st}) for Xe is 29 kJ/mol, significantly higher than 14 kJ/mol for Kr (Figure S6). This is not surprising because Xe atoms are larger in size, leading to better contact with the pore surface of compound **1**, which results in a higher adsorption affinity. The Q_{st} value for Xe is higher than those of many of the previously reported MOFs with high Xe/Kr selectivity, including cobalt formate[12] and SBMOF-2.[17] This indicates that the channel structure of compound **1** is optimal for the accommodation of Xe. The material adsorbs 57 cm³/g at 0.5 bar and 61 cm³/g at 1 bar and 298 K (roughly equivalent to 1 Xe atom per segment), compared to 18 and 29 cm³/g for Kr. The higher adsorption capacity and stronger adsorption affinity toward Xe renders compound **1** a promising candidate for the adsorptive separation of Xe/Kr mixtures. The adsorption selectivity toward Xe over Kr has also been evaluated quantitatively by ideal adsorbed solution theory (IAST) and Henry constants.

Using the Xe and Kr adsorption isotherms at 298 K, the calculated Xe/Kr IAST selectivity is 10.2 for a Xe:Kr = 20:80 (v/v) binary mixture with a total pressure of 1 bar. In addition, the Xe/Kr selectivity calculated by Henry constants gives a value of 12.5, with a Henry coefficient of 15.8 mmol/g/bar for Xe. This selectivity value is not as high as the recently reported $Co_3(C_4O_4)_2(OH)_2$ and MOF-Cu-H; however, it outperforms many prototype MOF materials such as HKUST-1, cobalt formate, etc. (Figure 3).[18] The high Xe/Kr adsorption selectivity of compound **1** can be attributed to the matching dimensions between its channel size and the atomic size of Xe.
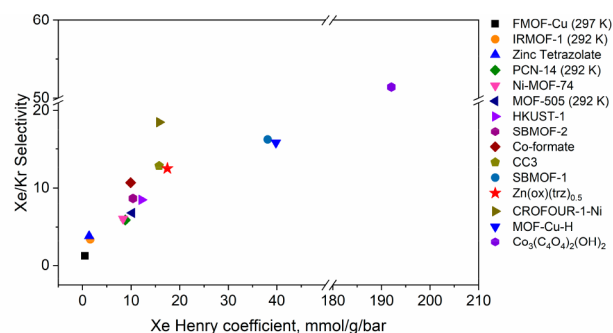

Figure 3. Survey of the Xe/Kr separation performance in reported materials. Henry coefficients were extracted from single-component adsorption isotherms at 298 K, unless otherwise specified.

To our surprise, compound **2**, the amino-functionalized analogue of compound **1** with a channel diameter of 2.12 Å, shows substantial adsorption toward Xe and Kr as well. However, its adsorption behavior is distinctly different from that of its parent compound. It displays notably stepwise adsorption with huge hysteresis loops toward Xe, as depicted in Figure 2, which has been commonly observed for MOFs with flexible networks.[19] This indicates that the added amino group leads to channel contraction as well as structure flexibility in compound **2**. In order to better understand the adsorption behavior of these two compounds, gas adsorption experiments at low temperature were performed. Because neither of the two materials adsorbs N_2 at 77 K, CO_2 adsorption measurements at 195 K were conducted instead. As shown in Figure S9, clear stepwise adsorption was observed for compound **2**, which is a characteristic adsorption profile for flexible MOFs. In contrast, under identical experimental conditions, the stepwise adsorption profile was not seen for compound **1**. The Xe adsorption capacity of compound **2** at 1 bar is similar to that of compound **1**, suggesting that the structure with Xe adsorbed would be similar to that of compound **1**. It is worth noting that the adsorbed amount of Xe on compound **2** is independent of the temperature at 278, 288, and 298 K because all three isotherms reach an uptake amount equivalent to ~1 Xe per segment (~4 Xe per unit cell), which is strong evidence of commensurate adsorption.[12] Commensurate adsorption of atomic Xe on compound **2** suggests the matching size of its channel with Xe atoms. Kr adsorption profiles in compound **2** are similar to those in compound **1**, indicating that the structure change was not induced by Kr under the tested pressure, which should take place at a higher pressure.

To verify the aforementioned experimental observations, computational modeling of gas adsorption using *Cerius2* sorption software (Accelrys Inc.) was performed. For a typical

simulation study for compounds **1** and **2**, supercells built on 4 × 2 × 2 unit cells were created. The simulation results are shown in Figures S10−S13. The low-temperature He adsorption simulation depicts the zigzag shape of the 1D channel in compound **1** with large chambers connected with small necks (Figure S11). The Xe adsorption simulation at 298 K reveals that Xe atoms are frozen at the chamber positions with an uptake of 1 Xe per segment, which agrees well with the experimental adsorption results. In contrast, under an identical simulation setup, Kr atoms are randomly distributed in the channels with low occupancy. This further confirms that the high Xe/Kr adsorption selectivity by compound **1** is a result of the match between the pore structure and atomic size of Xe. Adsorption simulations were also performed for compound **2**. As expected, no Xe or Kr adsorption was observed at 298 K and 1 bar. This is reasonable considering its effective pore size (2.02 Å). The framework needs to undergo a structural change to accommodate these molecules.

To evaluate the feasibility of using compounds **1** and **2** as candidates for the separation of Xe and Kr, dynamic breakthrough measurements for both materials were carried out at room temperature for a Xe:Kr = 20:80 (v/v) binary mixture, mimicking the real world separation. The break-through curves are shown in Figure 4. Compound **1** shows a
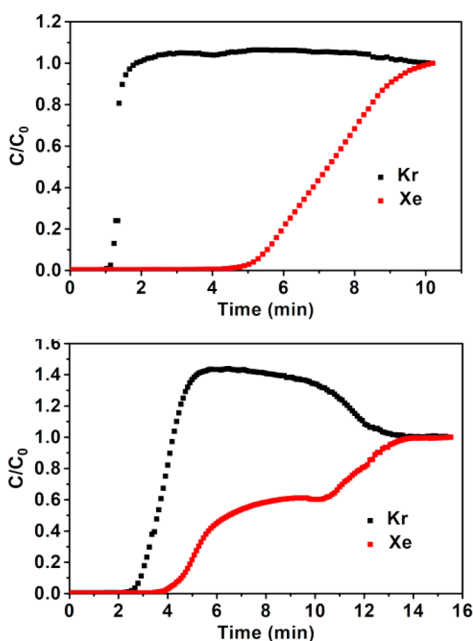

Figure 4. Column breakthrough curves for a 20:80 Xe/Kr binary gas mixture carried out on compounds **1** (top) and **2** (bottom) at 298 K and 1 bar.

nice separation for Xe and Kr. While Kr breaks out at the first minute and immediately reaches its feed concentration, Xe is retained in the column for more than 4 min before breaking out and does not reach its feed concentration until the 10th minute. It should be noted that the concentration of Kr at the outlet of the column exceeds its feed concentration in the first couple of minutes, indicating that the adsorbent shows a stronger adsorption affinity toward Xe, which displaces the adsorbed Kr atoms during the breakthrough process. For compound **2**, Xe is also retained in the column for a longer time than Kr, and again displacement of adsorbed Kr by Xe was observed, suggesting that Xe is preferentially adsorbed as

well. However, Xe and Kr are not as well separated as in the case of compound **1**, although with similar breakthrough times (3 min for Kr and 4 min for Xe). This is not surprising because, from their single-component adsorption isotherms, it is clear that at the Xe partial pressure of the feed gas in breakthrough measurements (0.2 bar) the Xe uptake is only 23 cm^3/g, substantially lower than the value for compound **1**, 46 cm^3/g. This leads to the relatively poor separation capability for compound **2**. It is generally realized that structure flexibility could sometimes benefit the adsorptive separation of gas mixtures, but not always. It largely depends on the separation conditions as well as the pressure needed to induce the structure change of the material.

In summary, two ultramicroporous MOFs, $Zn(ox)_{0.5}(trz)$ and $Zn(ox)_{0.5}(atrz)$, were synthesized and fully evaluated for the adsorption and separation of Xe and Kr. $Zn(ox)_{0.5}(trz)$ shows highly selective adsorption toward Xe over Kr with a Xe/Kr selectivity of 12.5. This is a result of the matching between its channel dimension and the atomic size of Xe. In contrast, upon amino functionalization, $Zn(ox)_{0.5}(atrz)$ exhibits contracted channels and structure flexibility, leading to stepwise adsorption profiles toward Xe and sacrificed Xe/Kr selectivity. This work demonstrates that pore dimension is crucial when using MOFs for the separation of Xe and Kr, and structure flexibility should also be taken into consideration when optimizing the pore size for such a separation process.

■ ASSOCIATED CONTENT

ⓢ **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b02449.

> Materials synthesis and characterization and adsorption simulation (PDF)

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