Robust Bimetallic Ultramicroporous Metal−Organic Framework for Separation and Purification of Noble Gases

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ABSTRACT: Noble gases, especially krypton (Kr) and xenon (Xe), are widely applied in diverse fields. Developing new techniques and adsorbents to separate and purify Kr and Xe is in high demand. Herein, we reported a bimetallic metal−organic framework (MOF) (NKMOF-1-Ni) which possesses a narrow pore size (5.36 Å) and ultrahigh stability (e.g., stable in water for 1.5 years). Gas sorption measurements revealed that this MOF possessed much higher uptake for Xe than for Kr, Ar, or N_2 at room temperature in all pressure ranges. The calculation of adsorption isosteric heat and Grand Canonical Monte Carlo simulation verified that NKMOF-1-Ni had a stronger interaction with Xe than other tested gases. The results of ideal adsorbed solution theory selectivity and simulated breakthrough further showed that NKMOF-1-Ni had an outstanding separation performance of Xe/Kr, Xe/Ar, and Xe/N_2. This study provides important guidance for future research to synthesize ideal sorbents to separate noble gases.
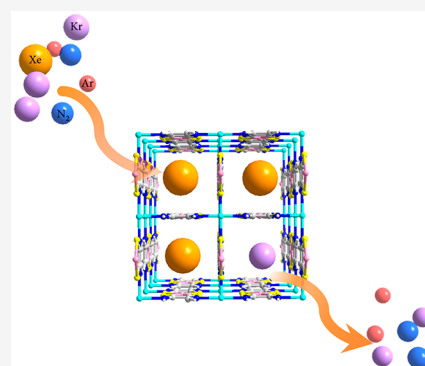
INTRODUCTION

Noble gases, including helium (He), neon (Ne), argon (Ar), krypton (Kr), and xenon (Xe), originated from the atmosphere and have low concentration therein.[1] The concentration of Ar (9340 ppmv) is much higher than that of He (5.2 ppmv), Kr (1.14 ppmv), and Xe (0.087 ppmv).[2,3] However, they all play essential roles in our daily lives and industrial production because of their stable physical and chemical properties. Noble gases possess plenty of industrial uses, including commercial lighting, as carrier gas, as insulation, and in imaging and anesthetics.[4] Among the noble gases, Kr and Xe have obtained widespread attention due to their broad application in diverse fields such as medical science and nuclear energy. Up to now, the price of high-purity Xe and Kr is ~$5000 per kilogram.[5] At present, the dominated technique to produce noble gases in industry is cryogenic distillation, which is based on the differences in boiling points of various gases (27 K for Ne, 87 K for Ar, 120 K for Kr, and 165 K for Xe).[6,7] In this process, air was liquefied first and then fractionally distillated in columns with different temperatures to obtain various gases such as N_2, Ar, Kr, and Xe. Despite this, Kr and Xe of high purity cannot be directly obtained but contain a 20/80 (v/v) mixture of Xe/Kr and Ar contaminate.[8,9] Meanwhile, this process is an energy-intensive and costly process. Nowadays, separation of Xe and Kr is still very challenging because of their similar boiling points (Xe: 165 K, Kr: 120 K) and close kinetic diameters (Kr: 3.7 Å, Xe: 4.1 Å).[7] Physical adsorption is an energy-saving technology which uses solid adsorbents to adsorb guests and can be carried out at room temperature.

Activated carbon, silica gel, zeolite, and molecular sieves are the common solid adsorbents which have been applied in gas separation, such as the separation of CO_2/N_2 and Xe/Kr.[10−12] However, they all have deficiencies, for instance, low selectivity and low capacity. Thus, developing new adsorbents which can surpass the traditional solid adsorbents is in high demand.

Metal−organic frameworks (MOFs) are a new class of functional porous materials which have attracted increasing attentions in the past two decades. MOFs consist of metal ion centers or metal clusters linked with organic building blocks via coordination bonds to produce diverse and customizable structural frameworks. Compared with traditional porous materials, MOFs have showed many advantages, such as adjustable pore aperture, high surface areas, and customizable structures. To date, MOFs have been applied in many fields, such as catalysis,[13−15] drug delivery,[16,17] sensors,[18] illumination,[19] batteries,[20] and gas storage[21−24] and separation.[25−29] Recently, several groups have carried out the separation and purification of noble gases by MOFs. In 2006, Pastre et al. first reported the separation of Xe and Kr by HKUST-1,[30] and further verified its selectivity by a binary gas mixture (Kr/Xe = 94/6) breakthrough at 40 bar and 328 K. In 2013, Li's group

reported a MOF named as $Co_3(HCOO)_6$ which can effectively separate Xe from other noble gases.[31] Along the same line, Thallapally et al. reported a hybrid ultramicroporous framework named as SIFSIX-3-Fe, which has both high selectivity of Xe/Kr and high gas uptake.[32] In terms of theoretical calculation, Sikora and coworkers generated over 13 700 hypothetical MOFs using thermodynamic analysis and found that the MOFs with pore size distributed 4.0−8.0 Å possessed higher selectivity over Xe/Kr than the MOFs with large pore size >10 Å.[33] Although the aforementioned MOFs have been applied for noble gas separation, they still suffer from some issues such as low stability and low uptake that limit their further applications. In this contribution, we reported a highly stable ultramicroporous bimetallic MOF (NKMOF-1-Ni) which showed high promise to separate noble gases (Xe, Kr, Ar, and N_2). This study provides important guidance for future researchers on how to design porous sorbents to separate noble gases.

EXPERIMENTAL SECTION

NKMOF-1-Ni was synthesized based on the literature procedure with slight modification.[34−37]

Synthesis of Na[Ni(pdt)$_2$·2H$_2$O]. Pyrazine-2,3-dithiol (pdt) (500 mg, 3.52 mmol) was added to 150 mL of acetonitrile with stirring for 2 h; NaOH (422.4 mg, 10.56 mmol) was dissolved in 10 mL of deionized water and then dropped into an acetonitrile solution with bubbling. After 2 h, $Ni(ClO_4)_2·6H_2O$ (658 mg) was added to the mixed solution and continued to bubble. After 3 h, 500 mg of I_2 was added, and the color of the solution changed from orange to green immediately. After stirring for 3 h, the solution was removed by vacuuming, and then 200 mL of acetone was added to dissolve the solid, which was then filtered by diatomite. Ether was added to precipitate solids.

Synthesis of NKMOF-1-Ni. Na[Ni(pdt)$_2$]·2H$_2$O (0.25 g, 0.62 mmol) was dissolved in acetonitrile (150 mL) and bubbled with argon for 30 min. CuI (0.142 g, 0.744 mol) was dissolved in acetonitrile (15 mL) and bubbled with argon for 30 min. Subsequently, CuI solution was slowly added into Na[Ni(pdt)$_2$]·2H$_2$O solution with stirring and bubbling. After 6 h, dark red powders of NKMOF-1-Ni were obtained by centrifugation and washed with acetonitrile five times. Before further tests, NKMOF-1-Ni was stored in MeCN.

RESULTS AND DISCUSSION

NKMOF-1-Ni possesses a 3-dimentional structure with ordered 1-dimentional (1D) channels extended along the *c* direction. The 1D square channels is ~5.36 Å (Cu···Cu distance after deducting van der Waals radius) (Figure 1). Powder X-ray diffraction (PXRD) pattern of the fresh sample matched well with the calculated PXRD pattern, indicative of the high purity of the as-synthesized sample (Figure S1). Water and thermal stability were essential for materials in real applications. According to the previously reported result,[34] NKMOF-1-Ni exhibited excellent thermal stability and can still maintain crystallinity after heating up to 240 °C. We further comprehensively studied the chemical stability of NKMOF-1-Ni. It was found that NKMOF-1-Ni can be stable in water for more than 1.5 years at room temperature, verified by PXRD (Figure S1) and BET surface area measurements. The BET and Langmuir surface areas of NKMOF-1-Ni soaking in water for 1.5 years were 365 and 545 m²/g, respectively, comparable
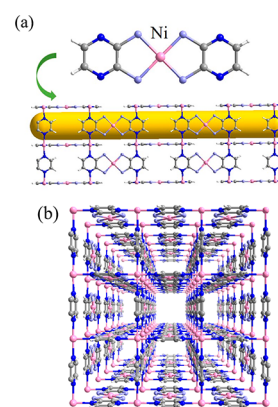

Figure 1. (a) The building unit of NKMOF-1-Ni. (b) The 3D structure of NKMOF-1-Ni with 1D channel along the *c* axis.

to those of the fresh sample (BET: 354 m²/g, Langmuir: 515 m²/g, shown in Figure S2). Meanwhile, we also tested the moisture stability of NKMOF-1-Ni. It was evidenced by the PXRD pattern (Figure S1) that NKMOF-1-Ni was stably stored at 70% humidity for at least 6 months. Moreover, we tested the stability of NKMOF-1-Ni in different solvents, and it was stable in methanol, dimethyl sulfoxide, acetone, dichloromethane, and ethyl acetate for at least 1 month, as verified by PXRD data (Figure S3). The narrow pores and excellent stability endowed NKMOF-1-Ni great potential for separation and purification of noble gases.

To explore the potential separation performance of NKMOF-1-Ni for noble gas separation and purification, we collected single-component adsorption isotherms of N_2, Ar, Kr, and Xe for NKMOF-1-Ni at 273 and 298 K, respectively (Figure S4). NKMOF-1-Ni was found to adsorb 0.16 mmol/g of N_2, 0.39 mmol/g of Ar, 1.20 mmol/g of Kr, and 2.16 mmol/g of Xe at 298 K and 1 bar (Figure 2b). Notably, the capacity of Xe was almost two times higher than that of Kr. In addition, we found NKMOF-1-Ni absorbed 0.25 mmol/g of N_2, 0.84 mmol/g of Ar, 1.86 mmol/g of Kr, and 2.47 mmol/g of Xe at 273 K and 1 bar (Figure 2a). Furthermore, we compared the adsorption capacity of each single component (N_2, Ar, Kr, and Xe) gas at low pressure (0.1 bar) and found the capacity of Xe, Kr, Ar, and N_2 were 0.98, 0.44, 0.08, and 0.03 mmol/g, respectively.

The coverage-dependent isosteric heats of adsorption (Q_{st}) can quantitatively assess the binding affinity of adsorbents toward different guest molecules. It was calculated based on single-component gas adsorption curves of NKMOF-1-Ni at 273 and 298 K. The single-component adsorption curves were fitted by Virial equation. Q_{st} values were calculated according to the Virial equation.[38,39] (Figure S5) The zero-coverage Q_{st} value of NKMOF-1-Ni was estimated to be 34.2 kJ/mol for Xe, which was higher than most reported MOFs, such as HKUST-1 (26.9 kJ/mol),[30] Ni-MOF-74 (22.0 kJ/mol),[40] SBMOF-2 (26.4 kJ/mol),[41] CROFOUR-2-Ni (30.5 kJ/mol),[42] UiO-66 (25.0 kJ/mol),[43] and $Co_3(HCOO)_6$ (28.0 kJ/mol).[31] The calculated Q_{st} at zero coverage is 33.1 kJ/mol for Kr, 26.1 kJ/mol for Ar, and 12.0 kJ/mol for N_2, respectively. These results demonstrated that NKMOF-1-Ni had obviously stronger interaction with Xe than other gases.

Adsorption selectivity is a factor to evaluate the separation performance of binary or multicomponent mixtures for an adsorbent. We calculated the gas mixture selectivity of NKMOF-1-Ni by using ideal adsorbed solution theory
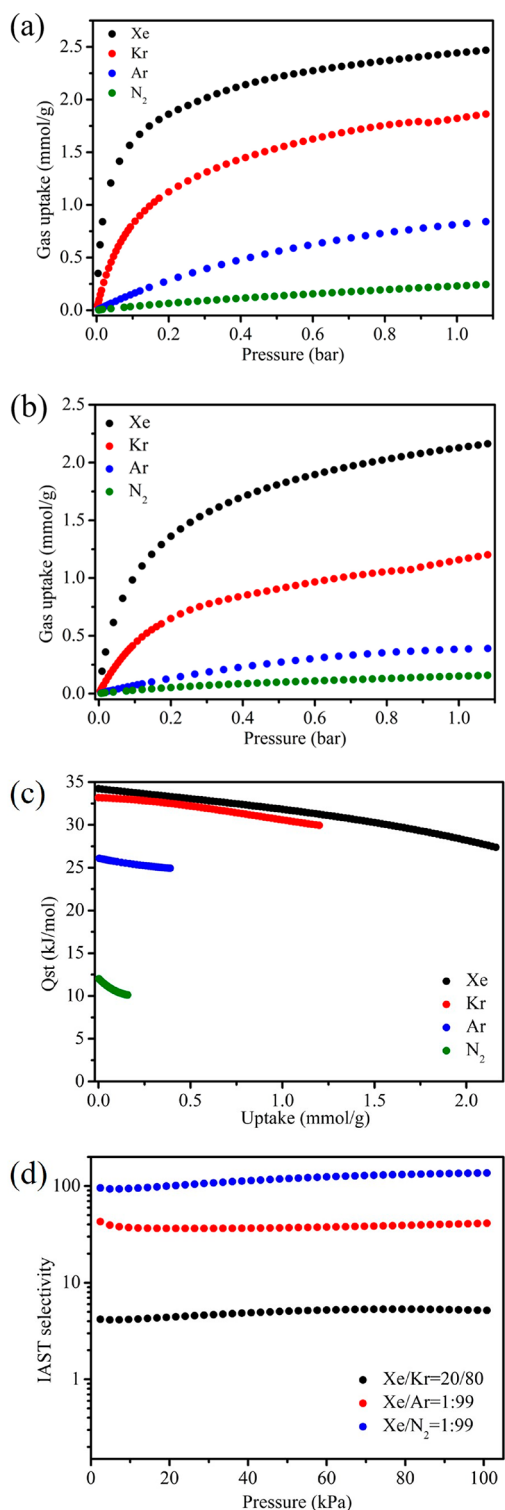
Figure 2. Single-component gas (N_2, Ar, Kr, and Xe) adsorption isotherms and selectivity of NKMOF-1-Ni. (a) The adsorption isotherms of NKMOF-1-Ni at 273 K. (b) The adsorption isotherms of NKMOF-1-Ni at 298 K. (c) Q_{st} curves of adsorption of NKMOF-1-Ni for Xe, Kr, Ar, and N_2. (d) The IAST selectivity of Xe/Kr (20/80), Xe/Ar (1/99), and Xe/N_2 (1/99).

(IAST) based on the single adsorption isotherms collected at 298 K and 1 bar. Before the selectivity calculation, we used the dual-site Langmuir−Freundlich equation to fit the single component adsorption isotherm curves for each gas. The

fitted parameters for each gas were displayed in Table S1. The IAST selectivities for Xe/Kr (20:80), Xe/Ar (1:99), and Xe/N_2 (1:99) are displayed in Figure 2(d). The calculated selectivity value for Xe/Kr (20/80) binary gas mixture was ~5.2, which is higher than those MOFs reported in the literature, such as IRMOF-1 (2.5−3),[44] MOF-74-Ni (4),[40,45] and HKUST-1 (2−3).[46] The selectivity of Xe/Ar (1/99) was 41.3 at 298 K and 1 bar and was 60 at low pressure. Moreover, the selectivity of Xe/N_2 (1/99) was 136.7 which is higher than those MOFs reported in the literature, such as HKUST-1 (52.35) and MOF-74-Ni (13.45).[45]

Theoretical simulation is a powerful tool which can unveil a lot of useful information behind the phenomena. To understand the interaction between noble gases and the frameworks of NKMOF-1-Ni, the noble gas adsorption property of NKMOF-1-Ni was studied by Grand Canonical Monte Carlo (GCMC) simulations.[47−50] The GCMC results revealed that the simulated Xe and Kr uptakes were 2.28 and 1.12 mmol/g, respectively, at 298 K and 1 bar. The results were close to the experimental results. A slice through the calculated potential field demonstrated there were two preferential adsorption regions in NKMOF-1-Ni (Figure 3),
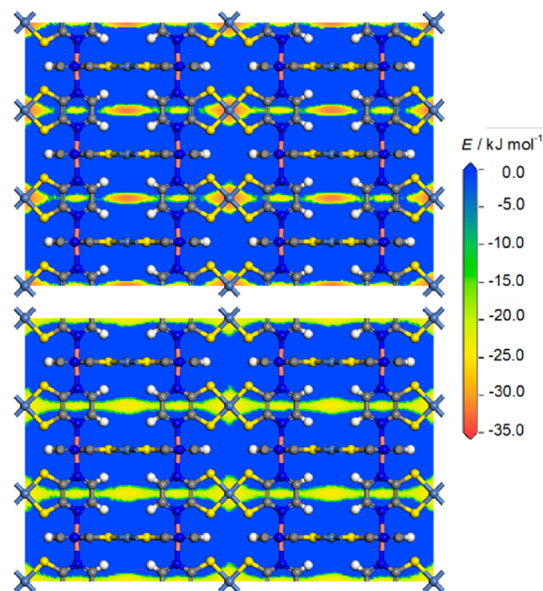

Figure 3. A slice through the calculated potential field for Xe (top) and Kr (bottom) in NKMOF-1-Ni. S: yellow, C: gray, N: blue, Cu: orange, H: white, Ni: navy.

the highest potential location was between the two open metal sites, and the other site was between two pyrazine rings. Therefore, the combination of open metal sites and conjugated pyrazine rings endows NKMOF-1-Ni with a strong interaction towards gas molecules.

We further investigated the gas mixture separation via simulated breakthrough experiments. Herein, we used a software associated with the 3P mixSorb Manager instrument named 3P Simulation to simulate the breakthrough of Xe/Kr (20/80), Xe/Ar (1/99), and Xe/N_2 (1/99).[51,52] Before monitoring the breakthrough curves, we fitted the single-component adsorption curves by the equation named DS langmuirSIPS (the fitted parameters are displayed in Table S4) and then chose the ISAT method with DSLAISIPS model to simulate the breakthrough curves. The coefficients involved in

the simulation are shown in Tables S5−S7. The results exhibited that Xe was preferentially adsorbed in the all binary gas mixtures (Figure 4a−c), and then Ar, Kr, and N$_2$ were eluted subsequently. Furthermore, we simulated the ternary
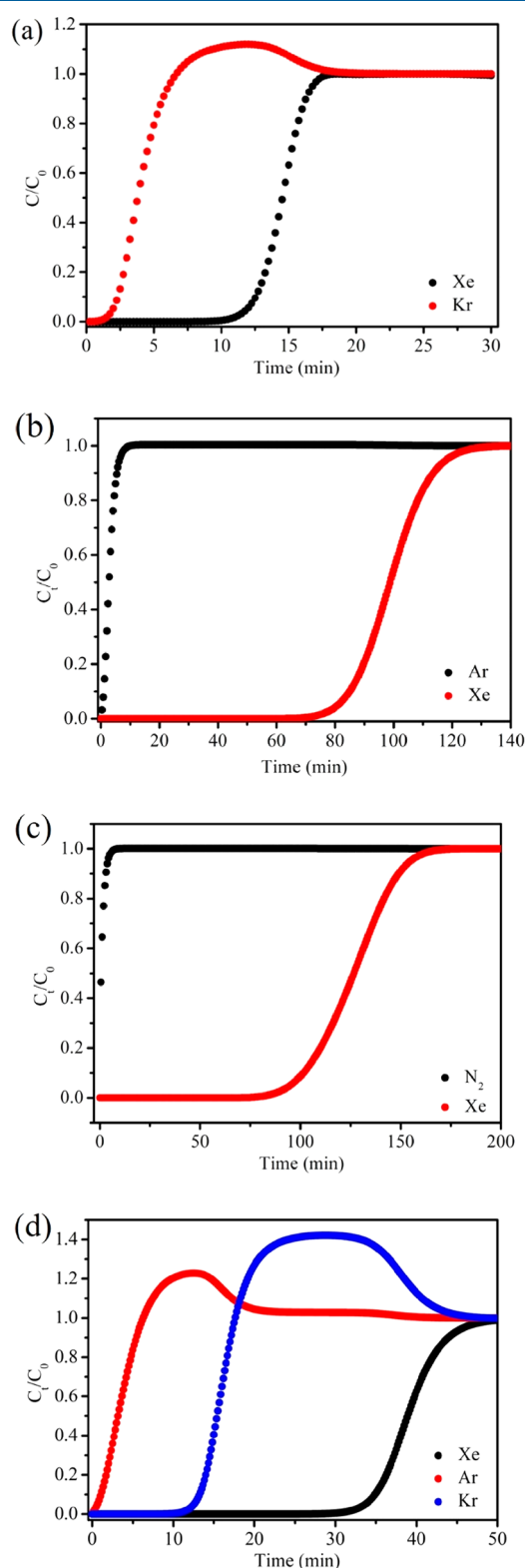
gas mixture (Xe/Kr/Ar = 1:1:1) breakthrough curve. The related parameters are displayed in Table S8. As shown in Figure 4d, Ar was eluted first, followed by Kr and finally Xe.

CONCLUSION

In conclusion, we reported a bimetallic MOF (NKMOF-1-Ni) which possessed narrow one-dimensional square channels and open metal sites benefiting the interaction with guest molecules. Single-component gas adsorption data and Q$_{st}$ calculation revealed that NKMOF-1-Ni has a stronger interaction with Xe than with Kr, Ar, or N$_2$. GCMC simulation revealed that the binding affinity can be ascribed to the two sites between gas molecules and frameworks. IAST selectivity calculation indicated that NKMOF-1-Ni has good separation performance on Xe/Kr, Xe/Ar, and Xe/N$_2$, which were further proved by simulated breakthrough curves of binary mixtures (Xe/Kr, Xe/Ar, and Xe/N$_2$) and a ternary mixture (Xe/Kr/Ar). Therefore, this work can guide future researchers to design ideal MOFs for noble gas separation and purification.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00134.

General materials, instruments, methods, PXRD results, and isotherm curves (PDF)

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Figure 4. Simulated breakthrough curves of noble gases. (a) Xe/Kr (20/80), (b) Xe/Ar (1/99), (c) Xe/N$_2$ (1/99), and (d) Xe/Kr/Ar (1:1:1).

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