

Control of Zeolite Local Polarity toward Efficient Xenon/Krypton Separation

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with a framework Si/Al ratio of 2.5 and Ca²⁺ as the counter-cations, namely, Ca-CHA-2.5, is developed as a state-of-the-art zeolite adsorbent, showing remarkable performance, i.e., high dynamic xenon uptake, high xenon/krypton separation selectivity, and good recyclability, in the adsorptive separation of the xenon/krypton mixture. Grand Canonical Monte Carlo simulation reveals that



extraframework Ca²⁺ cations act as the primary binding sites for xenon and can stabilize xenon molecules together with the chabazite framework, whereas krypton molecules are stabilized by weak guest-host interaction with the zeolite framework.

INTRODUCTION

The efficient separation of the xenon/krypton (Xe/Kr) mixture to obtain a high-purity single component is a critical industrial process due to their widespread applications in medical imaging, lasers, and aerospace technologies.^{1,2} However, the abundance of so-called rare gases in the atmosphere is extremely low (0.087 ppmV Xe, 1.14 ppmV Kr), and the direct extraction from air is very difficult.³ Currently, the cryogenic distillation of byproducts obtained from air separations (the concentrations of Xe and Kr are 20 and 80%, respectively) allows for the production of pure Xe and Kr streams. On the other hand, the isotopes of Xe and Kr are generated as volatile radionuclides during the reprocessing of used nuclear fuel (UNF). Compared to ⁸⁵Kr, Xe exhibits a relatively short half-life ($t_{1/2}$ = 36.3 days, 5.2 days, 9.1 h, and 10.8 years for ¹²⁷Xe, ¹³³Xe, ¹³⁵Xe, and ⁸⁵Kr, respectively), and it can be converted to a stable form after a period of storage.⁴⁻⁶ Consequently, Xe/Kr separation is also an essential step in the treatment of radioactive ⁸⁵Kr and provides an additional source of pure Xe stream.

Membrane-based separation and adsorptive separation are emerging as promising alternatives to energy-intensive cryogenic distillation. Zeolites, with ordered microporous channels, have shown versatile applications as membrane materials and adsorbents.⁸⁻¹⁰ By capitalizing on the slight difference in kinetic diameters (4.047 and 3.655 Å for Xe and

Kr, respectively), a variety of size-sieving zeolite membranes have been constructed to achieve efficient separation.¹¹⁻¹⁴ In contrast, the adsorptive separation necessitates suitable hostguest interaction regardless of the molecular sieving effect. That is, the target molecules should be, at least temporarily, reserved in the adsorbents to establish a distinct breakthrough time of different gases for effective separations. Xe and Kr are both monatomic inert gases, and their valence orbitals are fully filled with electrons, possessing zero dipole and quadrupole moments. Thereupon, traditional interaction forces such as dipole-dipole interaction and $\pi - \pi$ stacking are incapable of binding Xe and/or Kr to porous adsorbents, making the adsorptive separation of Xe/Kr extremely challenging.¹⁵ Fortunately, there exists a significant difference in the polarizability of Xe (40.44 \times 10⁻²⁵ cm³) and Kr (24.84 \times 10^{-25} cm³) that can be utilized for their separations. In principle, a suitable polarized environment might be applicable to Xe/Kr separations. By this means, metal-organic frameworks (MOFs) with open metal sites and/or polar groups have

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Figure 1. (a) Static adsorption isotherms of Xe on various Na-zeolites at 298 K. (b) Static adsorption isotherms of Kr on various Na-zeolites at 298 K. (c) IAST selectivity of Na-zeolites for the Xe/Kr (20/80, v/v) mixture. (d) Comparison of dynamic Xe uptake and Xe/Kr selectivity of Na-zeolites for the Xe/Kr (20/80, v/v) mixture. (e) Correlation between the polarization ability of Na-zeolites and the specific dynamic Xe uptake for the Xe/Kr (20/80, v/v) mixture. (e) Correlation between the polarization ability of Na-zeolites and the specific dynamic Xe uptake for the Xe/Kr (20/80, v/v) mixture.

shown promising performance in Xe/Kr separations.^{3,4,15–25} The selective adsorption of Xe can be achieved with zeolites containing noble metal atoms or nanoparticles, especially Agcontaining zeolites,^{7,26–30} in which the coordination of Xe to Ag originates from the strong polarization induction ability of metal species toward the electron-rich inert gas. However, Agcontaining zeolite adsorbents are expensive and the strong interaction between Xe and Ag-containing zeolites (isosteric adsorption heat >50 kJ/mol) poses further challenges for the regeneration of adsorbents. It is known that the polar environment of zeolites can be well tuned by changing the topology, framework composition (for example, Si/Al ratio), and counter-cations (alkali metal ions or alkaline earth metal ions), offering new opportunities to construct transition metal-free zeolite adsorbents for Xe/Kr separations.

Herein, through the control of local polarity, chabazite zeolite with a Si/Al ratio of 2.5 and Ca²⁺ as the countercations, namely, Ca-CHA-2.5, is developed as a robust transition metal-free zeolite adsorbent for efficient Xe/Kr separation. Typically, Ca-CHA-2.5 shows remarkable performance, *i.e.*, high dynamic Xe uptake, high Xe/Kr separation selectivity, and good recyclability, in the adsorptive separation of the Xe/Kr mixture, demonstrating its great potential for practical application. Significantly, the correlation between the local polarity of zeolite and the dynamic Xe uptake is established for the first time to guide the rational design of the adsorbent. The binding site and underlying mechanism of Xe adsorption are finally interpreted by the Grand Canonical Monte Carlo (GCMC) simulation.

RESULTS AND DISCUSSION

Various commercial zeolites in the Na form (Na-zeolites, the suffixal number indicates the Si/Al ratio; X-ray diffraction patterns shown in Figure S1), including chabazite (Na-CHA-2.5), SSZ-13 (Na-CHA-11.5), ZSM-5 (Na-MFI-13.1), X (Na-FAU-1.2), Y (Na-FAU-2.6), and beta (Na-BEA-13.4), were employed in the preliminary screening of efficient adsorbents for Xe. Static adsorption isotherms reveal that most samples exhibit higher saturated Xe adsorption capacity than Kr (Figure 1a,b and Figures S2-S5), probably due to the higher polarizability of Xe than that of Kr. The adsorption capacity of Xe varies widely among the samples. Na-CHA-11.5, Na-MFI-13.1, Na-FAU-1.2, and Na-BEA-13.4 exhibit relatively high Xe adsorption capacities ranging from 2.0 to 2.5 mmol/g. Following closely are Na-CHA-2.5 and Na-FAU-2.6, with adsorption capacities in the range of 1.0-2.0 mmol/g. Ideal adsorbed solution theory (IAST) was employed to predict the adsorption selectivity, and the calculated IAST selectivity of



Figure 2. (a) Correlation between the polarization ability of M-CHA-2.5 zeolites and the specific dynamic Xe uptake for the Xe/Kr (20/80, v/v) mixture. (b) Static adsorption-desorption isotherms of Xe and Kr on Ca-CHA-2.5 at 298 K. (c) Dynamic gas breakthrough curve of the Xe/Kr (20/80, v/v) mixture on Ca-CHA-2.5 at 298 K. Total gas flow= 5 mL/min. (d) Comparison of dynamic Xe uptake and breakthrough selectivity for the Xe/Kr (20/80) mixture on various solid adsorbents.

Na-zeolites for Xe/Kr mixtures (20/80) is shown in Figure 1c. Stronger interactions represented by the steeper Xe adsorption isotherm and the higher Xe/Kr IAST selectivity reveal the greater potential of the Na-CHA-2.5 zeolite in selective Xe capture. Considering the demand for Xe recovery in the byproduct from air separations and offgas from the UNF reprocessing process, dynamic breakthrough experiments were conducted under conditions of 20% or 400 ppm Xe in Xe/Kr mixtures at 298 K (Figure 1d and Figures S6-S11) and the dynamic adsorption performance is summarized in Table S2. Among all the samples investigated, Na-CHA-2.5 shows the best performance, i.e., the highest dynamic Xe uptake and breakthrough selectivity (Figure 1d), in good agreement with predictions from static adsorption. Notably, Na-zeolites with identical topology or similar Si/Al ratio display substantial variations in the dynamic adsorption capacity, e.g., at 20% Xe, CHA topology: Na-CHA-11.5 with 0.82 mmol/g versus Na-CHA-2.5 with 1.05 mmol/g; Si/Al of ~2.5: Na-CHA-2.5 with 1.05 mmol/g versus Na-FAU-2.6 with 0.3 mmol/g. These observations suggest that the dynamic adsorption capacity is regulated by a balance or combination of multiple factors such as the size of the confined space and framework composition.

The number of extra-framework cations, to balance the negative charges of [AlO₄] units in zeolites, is closely related to the polar environment of the zeolite pore interior, which in turn significantly influences the polarization ability toward noble gas molecules. Meanwhile, the dispersion force generated by the confined space within the zeolite pores shows noticeable impacts on the adsorption capacity. To clarify the relationship between the structure parameters of zeolites and the adsorption capacity, the concept of the polarization force parameter (Z) of cations (Z is the effective charge on the cation calculated by Sanderson's electronegativity equalization principle^{31,32}) was introduced.³³ Furthermore, the polarization ability of cations within the confined space of zeolites toward inert gases is supposed to be related to the number of ions (*n*: the number of cationic substances in zeolites) and the effective size of the confined space (*R*: the effective size of the confined space in cages, which is the ideal size without considering the cation occupation space). On the other hand, the microporous surface area (S: as Xe adsorption occurs dominantly on the microporous structure) and intrinsic properties of cationic species (mainly refers to valence state, X) are also important influencing factors. Overall, the dynamic Xe uptake (Q, when the diffusion issue can be simply ignored) of adsorbents is



Figure 3. Variation of Q_{st} and ΔS for Xe (a) and Kr (b) uptake in Ca-CHA-2.5 zeolite. (c) Temperature-programmed desorption profile of Xe in Ca-CHA-2.5 zeolite after saturated adsorption. (d) Concentration curves of Kr and Xe in the outlet during He purging at 333 K. (e) Recycling test of Xe/Kr (20/80, v/v) separation on Ca-CHA-2.5 zeolite. Adsorbent regeneration achieved by evacuation at 333 K for 30 min.

directly related to the polarization ability of zeolites (*F*, *F* \propto *Q*), and *F* should be a function theoretically related to *Z*, *n*, *R*, *S*, and *X*, *i.e.*, *F* = *f* (*Z*, *n*, *R*, *S*, and *X*). Herein, the dynamic uptake is normalized by the microporous surface area of samples, and the specific uptake per micropore area (*Q*_s) was employed to eliminate the impact from the microporous surface area (Tables S1 and S2). In this context, *Q*_s of Nazeolites is theoretically related to *Z*, *n*, and *R* {*Q*_s \propto *F*_{ZnR}, *F*_{ZnR} = *f*(*Z*, *n*, and *R*)}.

$$F_{\rm ZnR} \propto \frac{Z \times \sqrt{n}}{R^2}$$

The F_{ZnR} of Na-zeolites and Q_s were calculated and are summarized in Tables S2 and S3. Through data association, a good linear correlation is obtained, as shown Figure 1e. Significantly, the dynamic uptake or adsorption capacity can be regulated through the control of the zeolite local polarity. Generally, zeolite adsorbents with lower electronegativity of



Figure 4. Views of probability distributions of Xe within Ca-CHA-2.5 (a) and Mg-CHA-2.5 (b) zeolites at 298 K. Most probable Xe (c, e) and Kr (d, f) binding sites determined from GCMC simulation in Ca-CHA-2.5 and Mg-CHA-2.5, respectively. Ca: violet; Mg: pink; Si/Al: dark cyan; O: orange; Xe: red; Kr: navy.

Sanderson, higher cation contents (generally speaking, corresponding to lower Si/Al ratios), and smaller confined spaces should exhibit better performance for dynamic Xe capture. It should be noted that the window size of the confined space must be large enough to allow the free diffusion of Xe molecules, *i.e.*, to be significantly larger than the diameter of Xe. The pore size of Na-LTA-1.0 and Na-HEU-4.2 is too small to accommodate Xe guest molecules, and therefore, these two zeolites cannot adsorb Xe even under static conditions (Figure S5). Experimentally, Na-CHA-2.5 with an appropriate Si/Al ratio and confined space to construct a suitable polarized environment shows the highest dynamic Xe uptake among all Na-zeolite samples investigated (Figure S6).

Based on the above knowledge, it is possible to further improve the performance of CHA-2.5 by changing the countercations of zeolite. A series of alkali and alkaline earth metal ionexchanged CHA-2.5 zeolites (M-CHA-2.5; M = H, Li, Na, K, Mg, Ca, Sr, and Ba; X-ray diffraction patterns shown in Figure S12) were prepared and investigated for Xe capture and Xe/Ke separation (Figure 2 and Figures S13–S20). Typically, Li-, Caand Sr-CHA-2.5 zeolites exhibit superior Xe capture performance compared to Na-CHA-2.5, while H-, K-, Mg-, and Ba-CHA-2.5 show inferior performance. These results are in good consistency with static Xe uptakes in the literature report.³⁴ Large cations such as K⁺ and Ba²⁺ inevitably block the pore window of zeolite and hinder the free diffusion of Xe molecules (Table S1), resulting in the poor performance of K-CHA-2.5 and Ba-CHA-2.5 zeolites (Table S4). For other samples, good linear correlations between the specific dynamic uptake (Q_s) and the polarization ability (F_{ZnR}) that could be drawn are shown in Figure 2a. It should be noted that the linear correlation is highly dependent on the intrinsic properties of counter-cations and is generally applicable to elements of the same family. Remarkably, CHA-2.5 with Ca²⁺ as the countercations, i.e., Ca-CHA-2.5, exhibits very good performance in Xe capture and Xe/Kr separation (Figure 2). At a relative pressure of 0.2 bar (corresponding to 20% Xe), Ca-CHA-2.5 shows a high static Xe uptake of 1.75 mmol/g (Figure 2b), with an IAST selectivity exceeding 15 (Figure S21). Under the dynamic conditions with Xe concentrations of 20% or 400 ppm, Ca-CHA-2.5 exhibits high Xe uptakes (1.31 mmol/g for 20% Xe and 21.3 mmol/kg for 400 ppm Xe) with a selectivity of >12 (Figure 2b,c). The dynamic adsorption performance of Ca-CHA-2.5 is comparable to benchmark adsorbents such as Ni(4-DPDS)₂CrO₄,³ NiCo@C-700,¹⁶ and HOF-ZJU-202a⁴ (Figure 2d and Table S5). It should be emphasized that such

good performance is achieved with a low-cost (<\$2000/ton) and transition metal-free zeolite adsorbent {composition: Ca_{5.1}(Al_{10.2}Si_{25.8}O₇₂)}, which should be the ideal choice for practical application. In the presence of impurities such as water or carbon dioxide, the dynamic Xe uptakes decrease significantly, while the efficient separation of Xe/Ke can still be achieved with Ca-CHA-2.5 (Figures S22–S25).

The adsorption affinity of Xe and Kr in Ca-CHA-2.5 can be quantified by the adsorption heat from Henry's constants of adsorption³⁵ ($K_{\rm H}$, low-pressure region; Table S6) and Clausius-Clapyeron equation (Figures S26 and S27). The isosteric heats of adsorption (Q_{st}) of Xe and Kr were calculated to be 46.8 and 28.3 kJ/mol (Figure 3a,b), respectively, in good agreement with the binding energies from DFT calculations (Xe: 44.3 kJ/mol, Kr: 28.9 kJ/mol; Table S7). The significantly higher Qst of Xe adsorption than that of Kr demonstrates the stronger binding affinity of Xe than Kr and corresponds to the observed high Xe/Kr selectivity in a breakthrough experiment (Figure 2c and Table S5). Furthermore, the Q_{st} of ~45 kJ/mol should be an optimized value for Xe capture considering the balance between dynamic uptake, separation selectivity, and regeneration of the adsorbent. The temperature-programmed desorption profile of Xe on Ca-CHA-2.5 indicates that the desorption of Xe starts at a temperature of 313 K and ends at 353 K, with a peak at ~333 K (Figure 3c). In fact, Ca-CHA-2.5 can be fully regenerated by He purging or evacuation at 313 K for ~40 min (Figure S28). At a higher temperature of 333 K, the regeneration process is much quicker and can be accomplished within 10 min (Figure 3d). Xe with a purity of >99.9% can be collected after the complete desorption of Kr, and the productivities are 0.89 and 0.92 mmol/g through evacuation at 333 and 313 K, respectively. The intrinsic stability of zeolite and the unique Xe adsorption-desorption behaviors make Ca-CHA-2.5 an easy-recyclable adsorbent for Xe/Kr separation. As shown in Figure 3e, the dynamic Xe uptake and Xe/Kr selectivity remain completely unchanged along 20 cycles of breakthrough experiments.

To gain insights into the nature of host-guest interaction, GCMC simulations and DFT calculations were conducted on Xe and Kr adsorption on the best-performed Ca-CHA-2.5 zeolite (Figure 2) and poorly performed Mg-CHA-2.5 as a reference sample (Figure S17). The number of Xe and Kr molecules per unit cell used for DFT calculations and GCMC simulations is based on the adsorption capacities at 298 K. The probability distributions of Xe and Kr within Ca-CHA-2.5 and Mg-CHA-2.5 zeolite adsorbents are presented in Figures S29-S32 and Figure 4. Obviously, higher adsorption capacity of Xe and stronger adsorption strength of Xe than Kr were observed on Ca-CHA-2.5, consistent with the static and dynamic performance. Meanwhile, a much higher adsorption capacity of Xe was observed with Ca-CHA-2.5 than that with Mg-CHA-2.5. Both Xe and Kr were found to occupy the *t-cha* cage of Caand Mg-CHA-2.5, while they did not appear in the *t*-hpr (d6r)cage with the narrow window. The probable binding configurations of Xe and Kr in the t-cha cage of Ca-CHA-2.5 are further interpreted (Figure 4c,d and Figures S33 and S34). Typically, the Ca²⁺ is close to the six-membered ring connecting the t-cha cage and the t-hpr cage. The Xe atom binds to Ca^{2+} at a distance of 3.39–3.52 Å (Figure 4c), while the distance between Kr and Ca²⁺ is distinctly longer (3.61-3.78 Å; Figure 4d), indicating the presence of a weaker interaction. On the other hand, no significant strong

interaction between Mg^{2+} cations and Xe or Kr could be observed in Mg-CHA-2.5 (Mg...Xe: 3.70–4.00 Å, Mg...Kr: 3.95–3.98 Å), indicating that the guest molecules were mainly stabilized by framework through weaker interactions (Figure 4e,f and Figures S35 and S36). Generally speaking, the binding distance can indicate the strength of interaction, which is also consistent with the binding energy values from DFT calculations (Table S7). Hyperpolarized ¹²⁹Xe nuclear magnetic resonance spectroscopy further demonstrates the presence of strong interaction between Xe and Ca-CHA-2.5 (chemical shift at 180–210 ppm; Figure S37), in contrast to the Mg-CHA-2.5 zeolite. The above results reveal that although both Mg- and Ca-CHA-2.5 can accommodate Xe in the same *t-cha* cage of the topology, their local polarity dominates the adsorption strengths.

Derived from the difference in polarizability between Xe and Kr molecules $(40.44 \times 10^{-25} \text{ cm}^3 \text{ versus } 24.84 \times 10^{-25} \text{ cm}^3)$, corresponding to distinct interactions with the polarized environment, the control of the local polarity in zeolites can make the difference more pronounced and thereby achieve efficient separation. In the case of Ca-CHA-2.5, extraframework Ca²⁺ cations can serve as primary binding sites for Xe, inducing Xe polarization and resulting in efficient Xe capture. The enhanced adsorption performance using Ca²⁺ as the counter-cations of zeolite instead of Na⁺ can be also achieved with other zeolites like Ca-MFI-13.1 (Figure S38 and Table S2), confirming the key role of extraframework Ca^{2+} cation sites for Xe/Kr separation. It should be noted that the extraframework Ca²⁺ cation sites should work together with the zeolite framework to construct a suitable polarized environment in zeolite, i.e., the so-called local polarity, for Xe/Kr separation.

CONCLUSIONS

Xe capture and Xe/Kr adsorptive separation hold significant economic and environmental benefits as feasible alternatives to the energy-intensive process of cryogenic distillation, while Xe/ Kr adsorptive separation remains challenging due to the similar nature of these noble gases. By changing the topology, framework composition, and counter-cations, the polarized environment of zeolite, namely, local polarity, can be well regulated, offering the opportunity of constructing a low-cost and transition metal-free adsorbent for Xe/Ke separation. A linear correlation between the local polarity of zeolite and the dynamic Xe uptake is established for the first time. Experimentally, Ca-CHA-2.5 is optimized with state-of-theart performance in Xe/Kr breakthrough studies, showing high dynamic Xe uptake, high Xe/Kr selectivity, and perfect recyclability at the same time. GCMC simulation reveals that extra-framework Ca²⁺ cations act as the primary sites, which work together with the CHA framework to create a suitable polarized environment for Xe capture. Overall, a very simple but effective strategy of tuning the polarized environment of zeolite has been successfully developed for the separation of noble gases with different polarizability.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c13994.

Experimental details, materials and methods, characterization results including XRD, Ar adsorption-desorption, TPD and NMR, more adsorption and separation data, and theoretical calculations (PDF)

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Notes

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