

Correlating the Adsorption Preference and Mass Transfer of Xenon in RHO-Type Molecular Sieves

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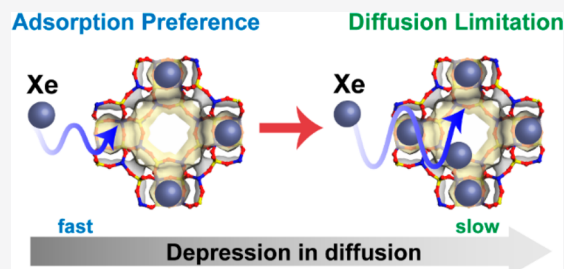
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ABSTRACT: The adsorption and diffusion of adsorbates or reactants are the most essential steps in zeolite-based processes for gas separation and catalysis. An explicit description of the relationship between adsorption and mass transport in confined environments of microporous materials is a prerequisite to catalytic reaction and gas separation. The dimensions, shapes, and types of pores are the most essential properties that govern the adsorption and diffusion behaviors of guest molecules. Here, a xenon atom was used as a sensitive probe to provide information about the dynamic adsorption process between the *lta* cavity and double eight-membered rings (D8R) of DNL-6 molecular sieves with RHO topology by ^{129}Xe NMR and pulsed field gradient (PFG) NMR. Loading-dependent ^{129}Xe NMR presents the two types adsorption environments with different probabilities of xenon distribution, and D8R is the preferential adsorption site. Furthermore, ^{129}Xe PFG NMR exhibits the mass-transport limitations of the xenon atom in DNL-6 as the loading increases. On the basis of molecular dynamics (MD) and Monte Carlo (MC) simulations, the interaction energies between RHO framework and xenon were predicted and the preferred adsorption character of D8R was displayed visually, which further contribute to the understanding of adsorption and diffusion behavior, especially for the loading dependence of intracrystalline diffusion. The diffusion limitation caused by the preferential adsorption of D8R can depress the mass transport in RHO-type molecular sieves. A direct relationship between the adsorption preference and diffusion was established at the molecular level.



1. INTRODUCTION

Mass transfer inside the confined spaces of zeolites and zeotype materials has attracted much attention from fundamental research and chemical engineering.^{1–5} This practical and theoretical interest has been motivated by the recognition that an in-depth understanding of mass transport results in better knowledge of practical applications of microporous materials as catalysts and adsorbents in catalysis and separation fields and also offers valuable information for the exploitation and further optimization of established zeolite-based processes.^{6–8}

In zeolite-based catalytic processes, the adsorption and diffusion of adsorbates or reactants are fundamental steps. For most sorbate–sorbent systems, the adsorption process is one of critical factors impacting mass transport.^{9–11} An underlying understanding of the adsorption process is a basic prerequisite for understanding mass transfer. A representative example of the significance of adsorption in the mass-transfer process is reflected in favorable adsorption sites.^{10,11} In this case, diffusion is mainly governed by the adsorption process. This issue, however, which has received far less attention in a single-component system, is a phenomenon worthy of attention and a

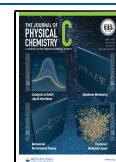
very interesting research topic. To correlate the adsorption character and diffusion behavior in a single-component system to obtaining a better understanding of mass transfer, we selected DNL-6 molecular sieves to adsorb xenon gas.

DNL-6 molecular sieves, consisting of a new eight-membered-ring (8-MR) silicoaluminophosphate, were first reported by our group for particular use in CO_2 separation and the methanol-to-olefins (MTO) process as an important shape-selective absorbent or catalyst.^{12–14} DNL-6 with an RHO framework has cubic symmetry ($Im\bar{3}m$, $a = 14.9 \text{ \AA}$), consisting of an *lta* cavity interconnected by double eight-membered rings (D8R) in three-dimensional directions. The D8R window is approximately a prism with an 8-MR window size of ca. $4.0 \times 4.3 \text{ \AA}^2$ and a thickness of $3.8 \text{ \AA}$ (Figure 1).

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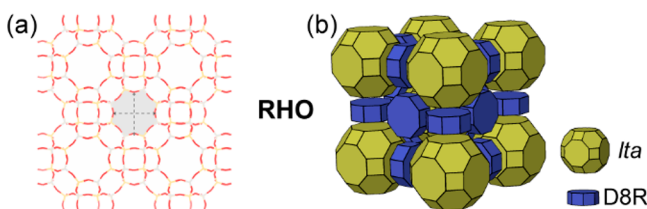


Figure 1. (a) Two-dimensional crystal structure viewed along [001] and (b) three-dimensional structure highlighted by yellow-filled *lta* cavities and dark-blue-filled D8R prisms of RHO. The size of the 8-MR window is $4.0 \times 4.3 \text{ \AA}^2$ (gray-filled), and the thickness of D8R is $3.8 \text{ \AA}$ (dark-blue-filled).

Depending on some external conditions including extraframework cations, temperature, and hydration, the RHO framework also shows small flexibility and adopts an acentric $I\bar{4}3m$ form, leading to the elliptical distortion of D8R.^{15–18} For H-RHO molecular sieves, it seems that the framework flexibility itself could be used to modify the pore size and shape without actually blocking these pores. And the unique RHO structure still providing two types of local spaces (*lta* cavity and D8R) was selected as a model to qualitatively determine the role of the confined effect of double eight-membered rings (D8R) on molecular adsorption and diffusion behavior.

As an inert guest atom, xenon was selected because its adsorption and diffusion processes in porous materials can be directly detected by ^{129}Xe NMR techniques. ^{129}Xe NMR is a nondestructive and extremely sensitive tool for probing the local chemical surroundings of porous media by correlating the confinement of xenon atoms with their chemical shifts.^{19–21} By an optical pumping method for the generation of hyperpolarized (HP) xenon, an enhancement of about 4 to 5 orders of magnitude in sensitivity can be realized after hyperpolarization, which allows a more sensitive detection of microporous materials.^{22–25} The use of pulsed field gradient (PFG) NMR for the measurement of the self-diffusion of guest molecules inside porous materials is well established.^{5,6,26–29} Moreover, the applications of Monte Carlo (MC) and molecular dynamics (MD) simulations enable visualized adsorption and diffusion processes in confined space and offer more useful information on the preferred adsorption site at a molecular level.^{4,30–33}

2. EXPERIMENTAL METHODS AND THEORETICAL CALCULATIONS

2.1. Sample Preparation and Characterization. DNL-6 molecular sieves were synthesized using a procedure reported in the literature.³⁴ The product was calcined at $600 \text{ }^\circ\text{C}$ for 5 h to obtain H-form molecular sieves. The powder X-ray diffraction (XRD) pattern of DNL-6 molecular sieves was obtained on an X-ray diffractometer with Cu $K\alpha$ radiation (PANalytical X'Pert PRO, $\lambda = 1.5418 \text{ \AA}$). The scanning electron microscopy (SEM) for the observation of crystal morphology and size was conducted on a Hitachi SU8020. An N_2 adsorption–desorption measurement was carried out at 77 K on a Micromeritics ASAP 2020.

2.2. Sample Pretreatment. Prior to NMR measurements, calcined DNL-6 molecular sieves were dehydrated at $420 \text{ }^\circ\text{C}$ for at least 15 h under high vacuum. Subsequently, the activated sample was transferred to a 5 mm outer-diameter NMR tube (ID = 3.5 mm, Wilmad-LabGlass) with a pressure valve used for ^{129}Xe NMR and PFG NMR in a glovebox. The

xenon-loaded samples used for PFG NMR were prepared by quantitatively introducing a known amount of xenon into the NMR tube on the uptake apparatus. Then the NMR tube was equilibrated at room temperature for at least 30 min and sealed off. The loading of adsorbate was calculated by using adsorbed xenon at very low pressure as an external standard which was determined by the ideal gas equation.

2.3. ^{129}Xe NMR. ^{129}Xe NMR was conducted on a Bruker AVANCE III 600 spectrometer at a resonance frequency of 166.1 MHz. A 5 mm diff50 NMR probe was used. One pulse sequence with 80 scans and a recycle delay of 8 s was applied.

2.4. Pulsed Field Gradient (PFG) NMR. A PFG NMR measurement was conducted on a Bruker AVANCE III 600 spectrometer at a resonance frequency of 166.1 MHz. A 5 mm diff50 probe was used, providing a gradient amplitude of 36–1800 G/cm in the Z direction. In diffusion tests, a stimulated echo sequence with bipolar gradients (also called a 13-interval) was adopted to eliminate the influence of magnetic susceptibility in beds of porous materials.^{5,26} Optimal parameters (δ , g , and Δ) were set for each PFG NMR test. The intracrystalline self-diffusion coefficient, D , is determined using eq 1

$$I = I_0 \exp \left[-(\gamma \delta g)^2 D \left(\Delta - \frac{\delta}{3} \right) \right] \quad (1)$$

where I_0 and I are signal intensities without and with gradient strength, respectively. γ refers to the gyromagnetic ratio of the ^{129}Xe nucleus, g is the gradient amplitude, δ is the effective gradient pulse duration, and Δ is the diffusion time.

2.5. Monte Carlo (MC) Simulation. The initial framework was built by substituting P and Al for Si atoms in a pure silicon RHO framework derived from the International Zeolite Association (IZA) database.³⁵ Centric space group $Im\bar{3}m$ was used on the basis of the X-ray diffractometry studies of the RHO zeolite with xenon atoms.^{36,37} The $3 \times 3 \times 3$ supercell structure was selected and optimized by GULP³⁸ with the SLC core–shell force field.^{39,40} In MC simulations using a Nosé–Hoover thermostat, the temperature was maintained at 298 K. The MC simulation was carried out at various loadings (1, 3, 6, and 11 loadings per unit cell). The simulation was equilibrated for 5×10^6 steps, followed by another 5×10^6 steps of production. After equilibration, the molecular trajectory was recorded each 50 cycles to form density maps, and the probability distribution of the adsorption energy⁴¹ was also recorded at each loading. All of the interactions in this system were described by a widely used universal force field (UFF).^{42,43}

2.6. Molecular Dynamics (MD) Simulations. The initial framework of molecular sieves used for our MD simulations is identical to that in the above MC simulations. In the simulations, the UFF was also applied. A Nosé–Hoover thermostat was employed to maintain the temperature at 298 K, with a time constant of 1 ps in the NVT ensemble. A Lennard-Jones potential was applied to model the host–guest interactions, with a $12.5 \text{ \AA}$ cutoff radius. The system was equilibrated for 3 ns followed by 20 ns of statistics, with a time step of 1 fs. The trajectories of the molecule were recorded every 1000 steps. For each system, three independent MD simulations are enough to obtain better statistics.

2.7. Diffusion Coefficient. On the basis of the MD simulations, the mean-square displacement (MSD) of the adsorbate is computed by the relation

$$MSD(\tau) = \frac{1}{N_m} \sum_i \frac{1}{N_\tau} \sum_{t_0}^{N_\tau} [r_i(t_0 + \tau) - r_i(t_0)]^2 \quad (2)$$

where N_m refers to the number of molecules and r_i indicates the location of the center of mass of molecule i . On the basis of the Einstein relation,⁴⁴ the self-diffusion coefficient, D_s , is determined from

$$MSD(\tau) = 2nD_s\tau + b \quad (3)$$

where n refers to the framework dimension ($n = 3$ for RHO). D_s was computed as the mean value of three independent MD trajectories by fitting the MSD curve in the linear region using a least-squares fit.

2.8. Interaction Energy. The interaction energy between xenon and the zeolite framework was calculated with the Forcite module along the diffusion path. The diffusion path is defined as a straight line in which one xenon atom moves from the center of one cavity to an adjacent cavity in 30 equally spaced steps. Detailed steps can be obtained in our previous study.⁴⁵

3. RESULTS AND DISCUSSION

The XRD pattern and SEM image indicate the good crystallinity of DNL-6 molecular sieves with a crystallite size of 10 μm (Figures S1 and S2). The preparation details of DNL-6 molecular sieves loaded with xenon are presented in the Experimental Methods and Theoretical Calculations section. Loading-dependent ^{129}Xe NMR spectra of DNL-6 molecular sieves measured at 298 K, as shown in Figure 2a,

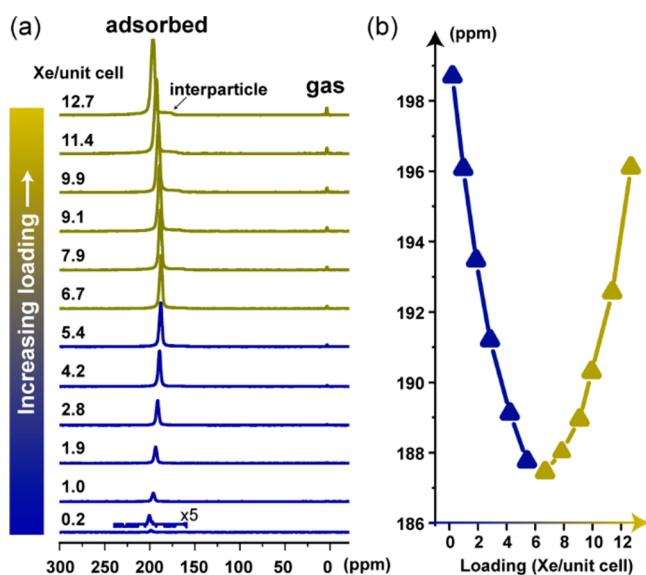


Figure 2. (a) Loading-dependent ^{129}Xe NMR spectra of DNL-6 molecular sieves obtained at 298 K. (b) ^{129}Xe NMR chemical shift of adsorbed xenon as the xenon loading increases.

include two types of resonance lines. The narrow peak at 0 ppm refers to xenon in the gaseous phase. And one symmetrical peak at lower field was assigned to xenon atoms confined in the pores of DNL-6 molecular sieves.^{46,47} A very broad signal with extremely low intensity at a higher field might be ascribed to xenon adsorbed inside mesopores from the interparticle. The chemical shift of xenon adsorbed inside DNL-6 varies with increasing loading, presenting a parabolic

trend (Figure 2b). The observed ^{129}Xe NMR chemical shift is a sum of different interactions on the NMR time scale.^{19,48} Typically, the dependence of the ^{129}Xe NMR chemical shift, δ , for xenon adsorbed in porous media on a number of different variables is summarized by the following expression^{19,48}

$$\delta = \delta_0 + \delta_s + \delta_{\text{Xe-Xe}} + \delta_{\text{SAS}} + \delta_M + \delta_E \quad (4)$$

where δ_0 is gaseous xenon at zero pressure, which is typically set to 0 ppm. δ_s refers to a xenon–surface interaction that is influenced by the pore dimension and shape. $\delta_{\text{Xe-Xe}}$ is the xenon–xenon interaction that is related to xenon density. δ_{SAS} displays the contribution from strong adsorption sites. δ_M and δ_E are ascribed to the presence of electric or magnetic fields. In the case of xenon adsorbed in DNL-6, δ_{SAS} , δ_M , and δ_E are negligible.

It is well established that the increased loading generally gives rise to a higher chemical shift due to strong xenon–xenon interactions for microporous solids with a single adsorption site.^{19,46,48} In the case of DNL-6 molecular sieves, at a loading of <6.7 atoms per unit cell, the chemical shift of adsorbed xenon decreases from 199 to 187 ppm as the loading increases. This goes against the normal rules in the case of a single adsorption site with an increase in xenon loading.^{46,48} Considering the structural features of DNL-6 molecular sieves, the D8R prism can contain one xenon atom with a kinetic diameter of 4.4 Å. Therefore, DNL-6 molecular sieves can provide two types of local spaces (an *lta* cavity and a D8R prism) for xenon adsorption. It is inferred that a decreased ^{129}Xe chemical shift with loading may be ascribed to the location variation of the xenon atom between two types of pore environments. The observation of a single peak of adsorbed xenon in the ^{129}Xe NMR spectra means that there is a very fast exchange between the *lta* cavity and the D8R prism due to these location sites being very close to each other. For such fast exchange, the observed average ^{129}Xe NMR chemical shift is a weighted average of xenon adsorbed in the *lta* cavity and D8R prism and can be written as^{19,46}

$$\delta = P_D\delta_D + P_C\delta_C = P_D\delta_D + (1 - P_D)\delta_C \quad (5)$$

where δ_C and P_C , δ_D and P_D refer to the chemical shift and probability of xenon adsorbed in the *lta* cavity and D8R prism, respectively.

A confinement effect imposed by topology on the xenon adsorption shall be considered first.⁴⁹ A small D8R prism, a more restricted space than the *lta* cavity, leads to strong xenon–surface interactions (that is, $\delta_D > \delta_C$) when xenon is adsorbed in DNL-6,^{19,21,50} which may be primarily responsible for xenon adsorption at 0.2 atoms per unit cell with a high ^{129}Xe NMR chemical shift value of 199 ppm. A decreased chemical shift with an increase in xenon loading indicates a decreased probability of xenon located at the D8R prism (P_D) and an increased probability of xenon located in the *lta* cavity (P_C). Considering that one RHO unit cell has two *lta* cavities and six D8R prisms and that one D8R prism contains no more than one xenon atom due to dimension limitations, the inflection point of the chemical shift with loading appears when six D8R prisms are completely filled with xenon atoms (i.e., the xenon loading reaches six atoms per unit cell). After that, as xenon loading increases from 6.7 to 12.7 atoms per unit cell, the peaks of adsorbed xenon gradually shift to lower field due to more and more xenon atoms in the *lta* cavity with an increase in xenon–xenon interactions. Therefore, such a nonmonotonicity alteration in the ^{129}Xe NMR chemical shift

of xenon adsorbed in DNL-6 as loading increases reveals the presence of two types of local adsorption environments with different probabilities of xenon distribution and that the D8R prism may be the preferred adsorption site.

To verify the above inferences about the xenon adsorption process and seek direct evidence of an adsorption preference in the D8R prism from a microscopic point of view, the interaction energy between xenon and the RHO framework was evaluated using a molecular dynamics simulation.⁵¹ The energy profile (Figure 3) presents the host–guest interactions

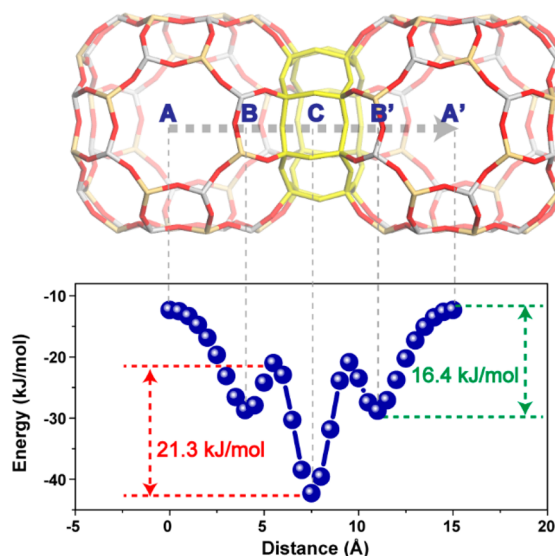


Figure 3. Energy profile of xenon at increasing distance when xenon is pulled from the center of mass of the cavity (A) to the center of mass of the adjacent cavity (A') passing through D8R windows within RHO. The RHO framework is colored gray (P atoms), gold (Al atoms), and red (O atoms). D8R is highlighted.

between xenon and the RHO framework as a function of the xenon position from the center of one cavity to the center of an adjacent cavity passing through D8R windows as the diffusion path. It is observed that the interaction energy between xenon and the RHO framework follows the order of $C > B (B') > A (A')$, which clearly shows that the center of the D8R prism (labeled as C) is the most favorable site for xenon adsorption in the RHO framework in terms of an energy maximum, followed by the edge of the *lta* cavity near the 8-MR window (labeled as B or B') and the center of the *lta* cavity (labeled as A or A'). Therefore, the D8R prism, presenting the largest interaction energy between xenon and the framework, serves as a preferred adsorption site during the adsorption process.

Furthermore, density distributions for xenon atoms residing in pores at different loadings are plotted in Figure 4 by Monte Carlo (MC) simulations. Density maps allow a good prediction of the positions of guest molecules in channels and the identification of preferred adsorption sites.⁵² The density distribution of adsorbed xenon in RHO at low and high loadings is different. At a low loading of 1.0 atom per unit cell, most of the xenon is mainly located in the center of the D8R prism, while a lower occupancy of the *lta* cavity is observed where xenon is less adsorbed. As the loading increases to 3.0 atoms per unit cell, besides xenon inside the D8R prism with the highest density, it can be seen that some xenon atoms also gradually move toward the edge of the *lta* cavity and close to the 8-MR window. More xenon atoms

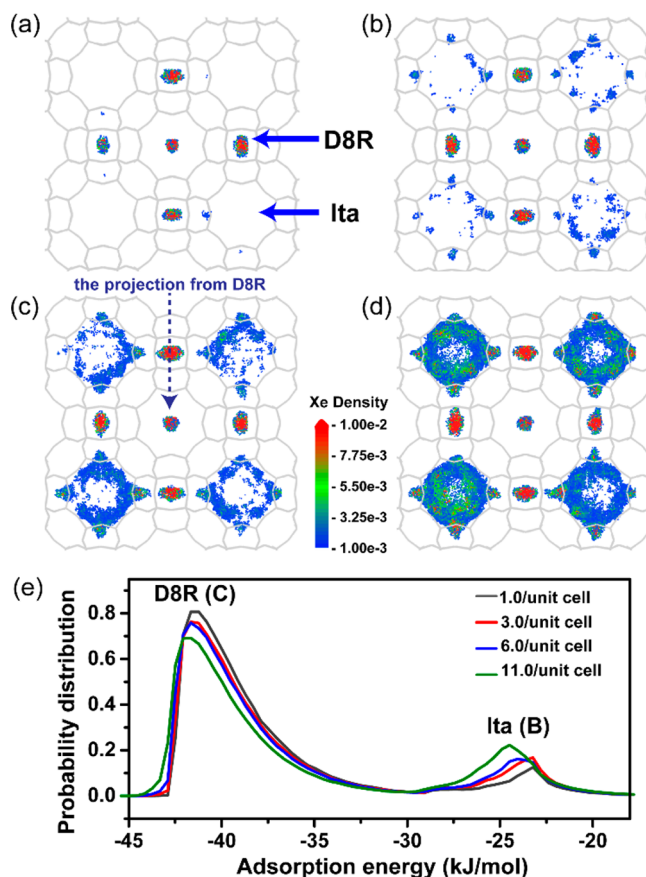


Figure 4. Density maps of xenon adsorbed in RHO at 298 K with increased loading (a) 1, (b) 3, (c) 6, and (d) 11 atoms per unit cell. The crystal structure of RHO is viewed along the [001] directions. The RHO framework is colored gray. The xenon density is represented by dots from blue to red. (e) Distribution probability of xenon in the D8R prism and *lta* cavity with variable loading. The positions of D8R (C) and *lta* (B) with maximum values of probability are shown in Figure 3.

reside on the edge of the cavity at higher loadings when D8R is filled with xenon. This finding leads to the conclusion that the D8R prism is more favored than the position near the 8-MR window. This observation agrees with the interaction energy result. Such a confinement effect of D8R on the adsorption of other molecules has also been confirmed in recent work.^{45,53} It should be especially noted that the observed red dots in the center of the *lta* cavity are attributed to the overlapped projection from xenon adsorbed in the D8R prism, and few xenon atoms are gathered at this location (Figure S3).

The dependence of the distribution probability in the D8R prism and the *lta* cavity of RHO on xenon loading is also predicted in Figure 4e. Two peaks from left to right represent the probability of xenon residing in the D8R prism and the *lta* cavity at a given loading, respectively. The probability of xenon located in the *lta* cavity increases as the loading increases, providing direct evidence for the variation in the chemical shift of xenon adsorbed in DNL-6 with loading. Moreover, the average adsorption of xenon in the D8R prism is always larger than that in the *lta* cavity (Figure 4e). This also means that a stronger xenon–surface interaction occurs in the D8R prism, contributing to the preferential occupancy of xenon. Such an observation further supports the fact that there are two types of

adsorption environments for xenon adsorbed inside DNL-6 molecular sieves.

To further correlate the adsorption behavior of xenon to intracrystalline diffusion and offers important insights about the role of the D8R prism in mass transport inside DNL-6 molecular sieves, ^{129}Xe PFG NMR results of DNL-6 are displayed in Figure 5. Figure 5a shows the recorded ^{129}Xe PFG

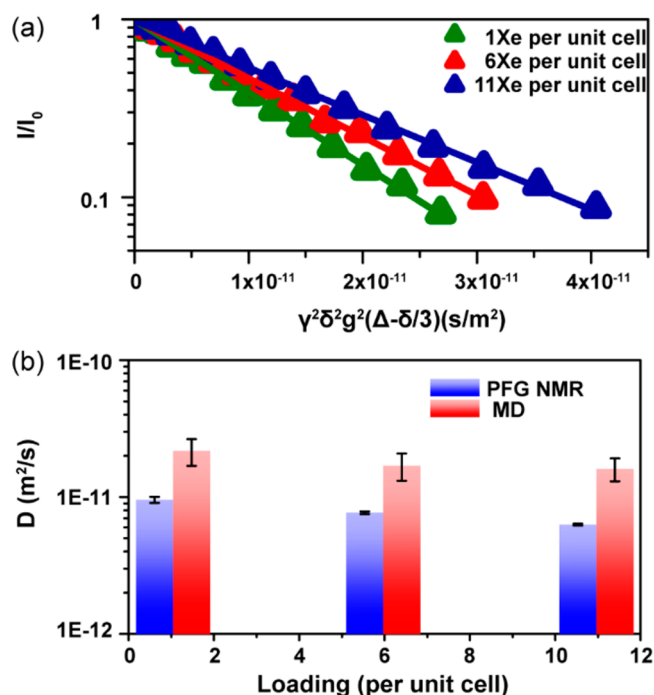


Figure 5. (a) Semilogarithmic plots of ^{129}Xe PFG NMR spin-echo attenuation $I(g)/I(0)$ of xenon inside DNL-6 molecular sieves loaded with, on average, 1, 6, and 11 atoms per unit cell as a function of $\gamma^2 \delta^2 g^2 (\Delta - \delta/3)$ recorded at 298 K, respectively. (b) Loading dependence on the self-diffusion coefficient of xenon adsorbed in DNL-6 at 298 K. The error bars are based on the standard errors.

NMR echo attenuation curves at 298 K for xenon in DNL-6 samples with different loadings. A linear fitting of the measured ^{129}Xe PFG NMR attenuation curves using eq 1 is presented on a log-linear scale, indicating that a single self-diffusion for xenon in DNL-6 is due to the rapid exchange between the *lta* cavity and D8R prism. A reduction in self-diffusion coefficients from 9.6×10^{-12} to $6.3 \times 10^{-12} \text{ m}^2/\text{s}$ as the xenon loading increases from 1.0 to 11.0 atoms per unit cell is shown in Figure 5b. It has been reported that one molecule that is strongly adsorbed in the window regions impedes the intercavity motion of other molecules in mixtures.^{10,11} In this work, the D8R, along with the edge of the *lta* cavity (B and B'), is considered to be the window regions for intercavity hopping due to the edge of the *lta* cavity (B and B') being very close to the eight-ring window, where xenon crosses from D8R to adjacent *lta* cavities, as depicted in Figures 3 and 4. As a result, it clearly indicates that the role played by loading in the self-diffusion coefficient is attributed to the preferred occupation of xenon in the window regions. Some xenon atoms that are preferentially adsorbed in the D8R prism hinder the intercavity motions of other xenon atoms inside the pores. Hence, xenon exhibits a decrease in the whole diffusivity with loading in DNL-6 molecular sieves. Moreover, the self-diffusion coefficient of xenon in RHO, calculated from MD

simulations (Figure 5b), also agrees with the PFG NMR results. Consequently, the diffusion study suggested that the preferred adsorption of xenon in the D8R prism induces a decreased diffusion with loading.

4. CONCLUSIONS

We have comprehensively studied the dynamic adsorption process and diffusion behavior of xenon in DNL-6 molecular sieves via ^{129}Xe NMR, ^{129}Xe PFG NMR, and theoretical simulations. It is disclosed that double eight-membered ring (D8R) windows serve as preferred adsorption sites for xenon adsorption. Furthermore, the preferred occupation of the D8R prism hinders the intercavity motions of partner xenon atoms, resulting in a reduction of the self-diffusion coefficient as the loading increases. The recognition of the Xe gas adsorption preference and mass-transport limitation of D8R windows would further lead to in-depth knowledge of mass transport in RHO-type materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c10813>.

XRD pattern and SEM image of DNL-6; density maps of xenon within RHO (PDF)

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Notes

The authors declare no competing financial interest.

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