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A density functional theory study for the adsorption of various gases on a caesium-exchanged trapdoor chabazite

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ABSTRACT

Rational design and development of porous materials for adsorptive gas separation gains ever-increasing attention as industrial applications, such as carbon capture and natural gas purification, always require more energy-efficient processes with adsorbents providing high selectivity. Zeolite molecular sieves represent a class of such desirable adsorbents. Our recently discovered molecular trapdoor mechanism in zeolites allows for unprecedented high selectivity and affords designability for versatile adsorbents. In this work, we presented a route for identifying the molecular trapdoor mechanism and predicting the gas separation feasibility using density functional theory calculations, based on a typical molecule trapdoor zeolite – caesium-exchanged chabazite with silicon to aluminium ratio of 3. We established criteria to assess the viability for "door-open" process by examining the dependence of energy barriers for the movement of "door-keeping" cation in the presence of different gases. Calculations at the standard PBE level and the van der Waals DFT levels were carried out. This theoretical route could serve as a standard method to study and develop other molecular trapdoor zeolites.

1. Introduction

Gas separations using microporous materials represents an ever-booming field, especially in recent years, as carbon capture attracts increasing attention due to the pressing concern on energy crisis and environmental protection [1,2]. For carbon capture, such an energy-efficient process requires high-performance adsorbents to selectively remove CO_2 from other molecules such as N_2, CH_4, H_2, and O_2. Zeolites serve as a primary class of candidate adsorbents for large-scale gas separations owning to multiple advantages such as high selectivity, low cost, as well as high thermal and mechanical stability [3]. These highly porous aluminosilicates possess three-dimensional structure of molecular dimension, thus being known as "molecular sieves". They could yield extremely high selectivity attributed to the molecular sieving effect: the host admits small guests in but excludes large ones out through its pore aperture [4].

However, this conventional explanation for the molecular sieving mechanism deserves a closer scrutiny when accounting for a host aperture coordinated by extraframework cations. In this case, a molecular trapdoor mechanism provides a more reasonable picture: a cation-kept zeolite aperture only exclusively admits certain molecules regardless of size [5–7]. We demonstrated this mechanism by investigating CO_2, N_2, and CH_4 separation on chabazite zeolites. Chabazite [8,9] features eight-membered ring (8MR) apertures that act as its only access for guest molecules; but in specifically tailored chabazites the guests are blocked by extraframework cations such as K^+ and Cs^+, which coordinate energetically favourably in the centre of the 8MRs. For a guest molecule to enter the supercavity, the door-keeping cation has to move away from the centre of the 8MR aperture. Our previous studies showed that CO_2 has "stronger" interaction strength with the door-keeping cations than N_2 and CH_4 molecules and thus can significantly flatten the potential well of the cation. At a certain temperature (corresponding to a certain kinetic energy value for the cation), the thermal excitation would lead to the temporary and reversible deviation of the cations away from the centre of the 8MR, giving way to CO_2 molecules to hop into the adjacent cages.

This novel molecular trapdoor mechanism opens up a new avenue for designing microporous materials with steered selectivity.

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However, a rational design requires detailed understanding at the atomic level, aside from trial and error procedures in the lab. Computer simulations provide indispensable tools to investigate and predict the physical chemistry properties at the atomic level. In this work, we employed density functional theory (DFT) calculations to study the molecular trapdoor mechanism occurring to a Cs-exchanged chabazite. Three typical small size gas molecules, CO_2, N_2, and CH_4 which are relevant to carbon capture applications, were adopted in our theoretical study. We established criteria to assess the viability of "door-open" process. In the end of this manuscript, the criteria were used to predict the selective adsorption of several other small gas molecules in the trapdoor chabazite. This work could afford a standard route for the theoretical design of the molecular trapdoor materials.

2. Methods

2.1. Structure model setup

Chabazite [8] consists of double-six ring (D6R) units arranged in layers that are linked together by tilted 4-membered rings (4MRs). The three-dimensional pore structure comprises large ellipsoidal supercavities of 6.7 × 10 Å, each of which is accessed by six eight-membered rings (8MRs) of 3.8 × 3.8 Å (Fig. 1). Previous studies [10–12] have shown that four types of general extraframework cation sites exist in dehydrated chabazite: one at the centre of the D6R prism (SI), one at the triad axis of the D6R prism but displaced to the supercavity (SII), one in the supercavity at the corner of the 4MR window of the D6R (SIII), and one at the centre of the 8MR window (SIII′).

Pure-silica chabazite was adopted as the starting point where the structural parameters for a conventional unit cell (referred to as unit cell hereafter), which consists of three double six-ring prisms or one and a half chabazite supercages, were taken from an experimental work [13]. Specifically, $a = 13.92779$ Å, $b = 13.94511$ Å, $c = 15.12131$ Å, $\alpha = 90.0929°$, $\beta = 89.9757°$, $\gamma = 120.3650°$. To introduce extraframework cations such as K^+ and Cs^+ into chabazite, a certain amount of silicon atoms were replaced by aluminium atoms to generate negatively charged chabazite frameworks with Si/Al ratio of 35:1 (**r35**CHA) and 3:1 (**r3**CHA), respectively. The unit cell formula is $K_1[Al_1Si_{35}O_{72}]$ for **r35**KCHA, $Cs_1[Al_1Si_{35}O_{72}]$ for **r35**CsCHA, and $Cs_9[Al_9Si_{27}O_{72}]$ for **r3**CsCHA. In our study, the **r35**CHA was used to determine cation site preference, which could be directly compared with literature results. The **r3**CHA represents our experimentally investigated chabazite counterpart, in which the trapdoor mechanism is enabled by considering the cations at relevant sites (SIII′) [5].

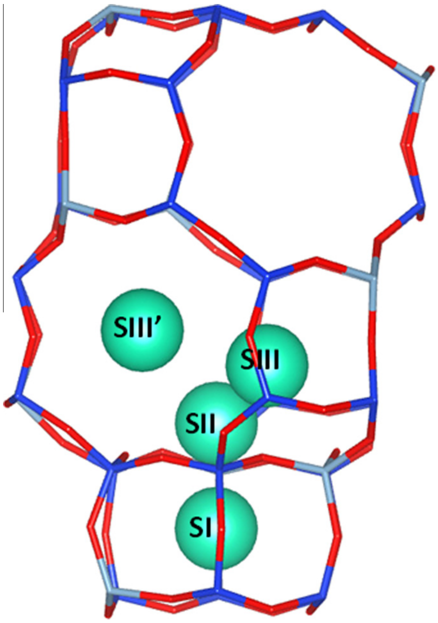

Fig. 1. Schematic representation of chabazite crystal structure and the extraframework cation sites. Double-six ring prisms (D6Rs) connected by tilted four-membered rings (4MRs) form a three-dimensional structure, generating eight-membered rings (8MRs) as the only access to the crystal interior. Four sites exist for extraframework cations: inside the centre of a D6R (SI); inside the supercavity above a D6R (SII); inside the supercavity next to a 4MR (SIII); in the centre of an 8MR (SIII′). Colour scheme: Red, O; Blue: Si; Grey, Al; Aqua, Cs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Given that the Al atoms introduce negative charges into chabazite frameworks, the extraframework cations were initially placed at the cation sites in the vicinity of Al atoms in our DFT calculations. For either **r35**KCHA or **r35**CsCHA, since there is only one Al per unit cell, we placed this Al at an intersection of an 8MR, a 6MR, and a 4MR. This allows us to generate a structure with a K^+ or Cs^+ cation placed at each of the possible cation sites (see Fig. 1 for details). By comparing the total energy results (E_{total}) of the obtained different crystal structures, i.e., the total energy with the cation at site SI (E_{total}(SI)), the total energy with the cation at site SII (E_{total}(SII)), E_{total}(SIII), and the total energy with the cation at site SIII′ (E_{total}(SIII′)), we could determine the site preference as per the rule, i.e., a higher total energy value indicates an unfavourable cation site. In the case of **r3**CsCHA, there are many different ways to place the 9 Al atoms in one unit cell. In order to calculate the energy barrier for Cs^+ cation migrating from site SIII′ to site SII with different number of Al atoms in the corresponding 8MRs and 6MRs, we considered all the possible Al distributions (Fig. 5).

For the gas–chabazite complex calculations, the structures were generated by placing a certain loading of gas molecules next to the target cations in supercavities of chabazite crystals. The gas molecule positions were selected so that both cation–gas and gas–gas distances were approximately 3.0 Å.

2.2. Computational setup

Ab initio density functional theory (DFT) calculations were employed to determine the chabazite structure, cation location and occupancy, as well as gas adsorption configuration. We used the Vienna *Ab initio* Simulation Package (VASP) [15] with the generalized gradient approximation (GGA) [16] and the projector augmented waves (PAW) approach [17]. The cut-off energy of the plane wave basis-set was 600 eV. A gamma point only *k*-point mesh was used for one unit cell of chabazite (including three double-six ring prisms or one and a half chabazite supercage). Such cut-off energy and *k*-point mesh have been tested to ensure the total energy convergence within 1 meV/atom. The atomic positions were optimized with the conjugate gradient method until the forces acting on atoms were below 0.015 eV/Å, as suggested by Göltl and Hafner [14]. We applied the nudged-elastic-band (NEB) method [22] for energy barrier calculations.

For the bare chabazite systems, the crystal structure were fully relaxed at PBE level since the dominant interaction in chabazite is the covalent bonding between silicon/aluminium and oxygen atoms and van der Waals dispersion interactions do not play an important role [14]. To more accurately account for the van der Waals interaction in the gas–chabazite complexes, dispersion-corrected DFT calculations with the optB86b-vdW functional scheme [18–20] was adopted because this scheme was determined to be the most appropriate one in our gas–chabazite system in a previous study [21]. Note that in our optB86b-vdW functional