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Original Research Article

Effect of Si/Al Ratio on Competitive CO_2/H_2O Adsorption in FAU Zeolite for Humid Flue Gas Capture: A Computational Study

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Abstract

Carbon capture from humid flue gas is problematic. Many microporous adsorbents are poisoned by water vapor. This research aims to study the effect of the Si/Al ratio on the competitive adsorption of CO_2 and H_2O in FAU-type zeolites, as well as evaluate their performance in capturing humid flue gases. Grand Canonical Monte Carlo (GCMC) simulations were performed to study the competitive adsorption of equimolar CO_2/H_2O mixtures at 298 K in two FAU zeolites: Zeolite 13X (Na_{77}, Si/Al ≈ 1.5) and Zeolite Y (Na_{49}, Si/Al≈2.92). The results showed that Zeolite 13X shows higher adsorption of CO_2 under low pressures, with the phenomenon of the roll-over occurring in the case of high pressure because of competitive adsorption with H_2O. In turn, the adsorption of CO_2 for Zeolite Y remained stable over the entire pressure range and exhibited lower H_2O uptake. Isosteric heats of CO_2 adsorption on the zeolites are 15.71 kcal/mol for Zeolite 13X and 13.23 kcal/mol for Zeolite Y. The energy of CO_2 binding in the presence of H_2O decreased by 1.14 kcal/mol for Zeolite 13X and for 2.03 kcal/mol for Zeolite Y. These findings indicate that high-silica FAU zeolites, such as Zeolite Y, are efficient CO_2 adsorbents.

Keywords: FAU zeolite; GCMC simulation; carbon capture; competitive adsorption; humidity effect

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1. Introduction

Carbon capture and storage (CCS) is one of the main tools we have to cut down greenhouse gas emissions [1]. Flue gases from industry carry a lot of CO_2, but they also come with 5–15 % water vapor. That water makes adsorption-based separation tricky because water molecules have a strong dipole and stick much more strongly to polar surfaces than CO_2 does – CO_2 only has a weak quadrupole [2 ,4].

FAU type zeolites, especially Zeolite 13X, are widely used for gas separation. They have large cages and, when dry, they take up a lot of CO_2 [3,5,7]. However, 13X has a low Si/Al ratio (about 1.5), so it needs many Na^+ ions to balance the negative charge from aluminum. The presence and distribution of Na^+ cations strongly influence adsorption interactions in sodium-exchanged faujasites [24]. As a result, water quickly saturates the pores, blocks them, and causes a sharp drop in CO_2 uptake – what the literature often calls the "roll over" or water poisoning effect [6,8]. On the other hand, when you go to a higher Si/Al ratio, like in Zeolite Y, you need fewer cations. This cuts down the hydrophilicity and helps maintain CO_2 capture even in wet streams [9]. This behavior was clearly proved through experiments; but in experiments, mainly the total uptake is studied without considering the sequential competitive processes taking place inside the pores on a molecular level. Current literature lacks molecular-level investigations investigations at the molecular level to understand the complex process of competitive

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adsorption of CO_2 and H_2O within FAU zeolites in humid environments [10,11]. To address this gap, Grand Canonical Monte Carlo (GCMC) simulations were performed to study the competitive adsorption of the equimolar CO_2/H_2O mixture in Zeolites 13X and Y and the corresponding isosteric heats of adsorption [12-14]. Unlike most previous studies which focused on reporting the total adsorption capacity, the present work provides a molecular-level analysis of competitive adsorption, the 'roll-over' phenomenon, and the effect of the Si/Al ratio on adsorption stability and regeneration energy [10-15]. Therefore, the main objective of this study is to assess the effect of the Si/Al ratio on the competitive adsorption of CO_2 and H_2O in FAU zeolites and to provide theoretical guidance for the selection of efficient adsorbents for moist flue gas capture [15].

2. Method: Computational Models

2.1. Zeolite Structures

In this simulation study, the following two zeolite FAU frameworks have been made:
- Zeolite 13X : Na_{77}, $Al_{77}Si_{115}O_{384}$, Si/Al ≈ 1.5. Molar mass ≈ 13,214 g/mol.
- Zeolite Y : Na_{49}, $Al_{49}Si_{143}O_{384}$, Si/Al ≈ 2.92. Molar mass ≈ 12,598 g/mol.

In the next step, Na^+ cations, in addition to being placed in the known crystallographic positions, were adjusted in the framework during a short geometry optimization [16,17]. In the subsequent GCMC, both zeolite framework and cations were kept rigid. Figure 1 shows the extra-frame Na^+ cation distribution in the zeolite frameworks.

2.2. Simulation Method

All Grand Canonical Monte Carlo (GCMC) simulations were run with the Sorption module in Materials Studio 2020 [27-30]. An equimolar mixture of CO_2 and H_2O (50 % each) was analyzed at 298 K and a fugacity range of 10 to 100 kPa. For these simulations, gas phase fugacities were calculated with the Peng-Robinson Equation of State [26]. Further, pure CO_2 simulations (without H_2O) were conducted at the same conditions for comparison.

2.3. Force Field

The COMPASSIII force field was used for all interatomic forces [20]. Carbon dioxide and water molecules were treated as neutral molecules, with partial charges assigned using the force field to accurately simulate electrostatic interactions [21,25].

2.4. Simulation Conditions

Electrostatic: Ewald sum (accuracy 0.0001 kcal/mol).
Van der Waals: Atomic cubic function, cut off at 15.5 angstroms [22].
For each active site: 100,000 equilibrium steps, followed by 500,000 production steps [23].

2.5. Calculation of Isothermal Heat

The isosteric heat of adsorption (Q_{st}) was calculated directly from the adsorption simulations by using the fluctuation method, which relates fluctuations in the number of adsorbed molecules to the energy of the system

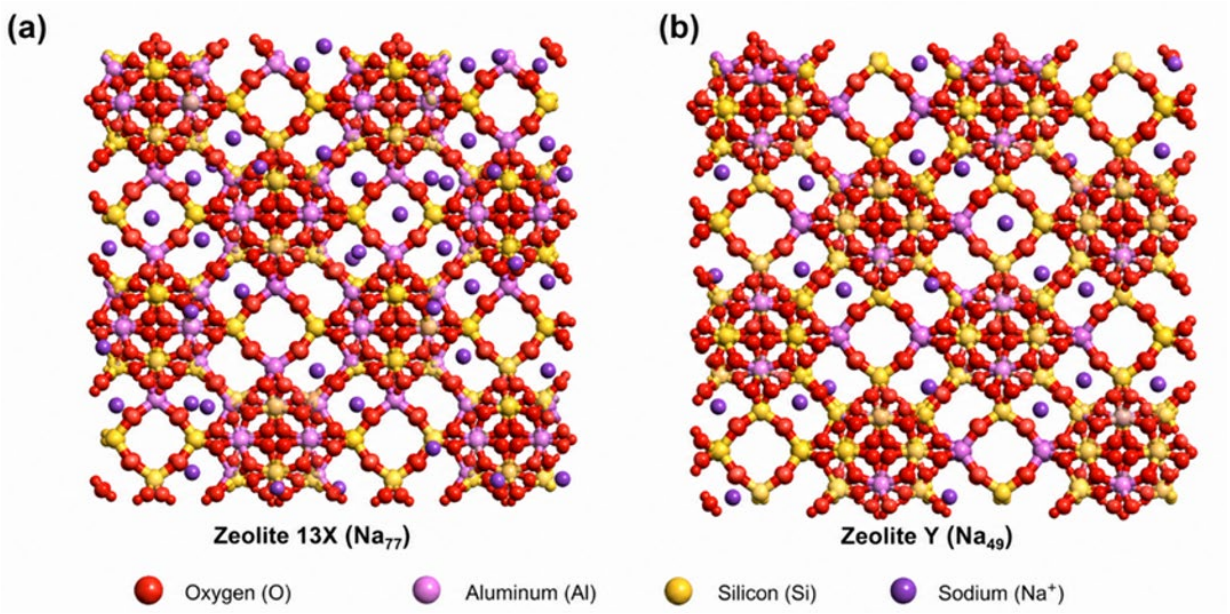

Figure 1. Atomistic representation of the FAU unit cell showing the distinct distribution of extra framework Na^+ cations in (a) Zeolite 13X (Na_{77}) and (b) Zeolite Y (Na_{49}).

[31,32]. The equation, using the fluctuation method for the Grand Canonical ensemble, is given below:

$$Q_{st} = RT - \frac{\langle UN \rangle - \langle U \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} \quad (1)$$

Where Q_{st} is the isosteric heat of adsorption, R is the universal gas constant, T is the absolute temperature, U is the configurational energy of the adsorbed molecules, N is the number of adsorbed molecules, $\langle UN \rangle$ is the ensemble average of UN, $\langle U \rangle$ is the ensemble average of U, and $\langle N^2 \rangle$ is the ensemble average of N^2.

3. Results and Discussion

3.1. Pure CO_2 Adsorption

Figure 2 shows the pure CO_2 loading as a function of pressure for Zeolite 13X and Zeolite Y at 298 K. For both zeolites, CO_2 loading increased with pressure, indicating favorable adsorption behavior over the investigated pressure range. Zeolite 13X also exhibited higher CO_2 uptake with approximately 132 molecules/cell at 100 kPa, compared with approximately 125 molecules/cell in Zeolite Y. The higher loading for Zeolite 13X is attributed to the higher density of Na^+ cations, which means more electrostatic adsorption sites for CO_2 molecules for Zeolite 13X. The results further indicate that the CO_2 adsorption of Zeolite 13X is higher than Zeolite Y because of its lower Si/Al ratio and higher cation density [5,7,9,24].

3.2. Competitive Adsorption in a Mixture

Table 1 shows the average adsorption capacities and thermodynamic properties at 100 kPa for a carbon dioxide/water mixture. The values are the mean ± half the range (minimum–maximum) to illustrate the statistical variation. Unlike pure CO_2 (Figure 2), the addition of water significantly affects the loading. Figure 3 shows the dynamic curves of the loading process. For Zeolite 13X, there is a significant maximum of the loading capacity of CO_2 at 55 kPa (about 65 molecules per cell), after which the value falls to 63.12 molecules per cell at 100 kPa. Simultaneously, the water loading grows from 120 to 132 molecules per cell under the same pressure conditions. Zeolite Y demonstrates totally different trends of the loading process. It retains

Table 1. Mean adsorption capacities and equilibrium properties for an equimolar carbon dioxide/water mixture at 298 K and a total pressure of 100 kPa.

Property	Zeolite Y (Na_{49})	Zeolite 13X (Na_{77})
H_2O loading (molecules/cell)	125.96 ± 3.0 (124–130)	132.22 ± 3.0 (130–136)
CO_2 loading (molecules/cell)	54.75 ± 2.5 (53–58)	63.12 ± 1.0 (62–64)
Average Q_{st} H_2O (kcal/mol)	17.12 ± 14.2 (1.19–29.59)	17.08 ± 12.4 (3.69–28.49)
Average Q_{st} CO_2 (kcal/mol)	13.23 ± 9.3 (2.39–20.99)	15.71 ± 9.05 (3.99–22.09)

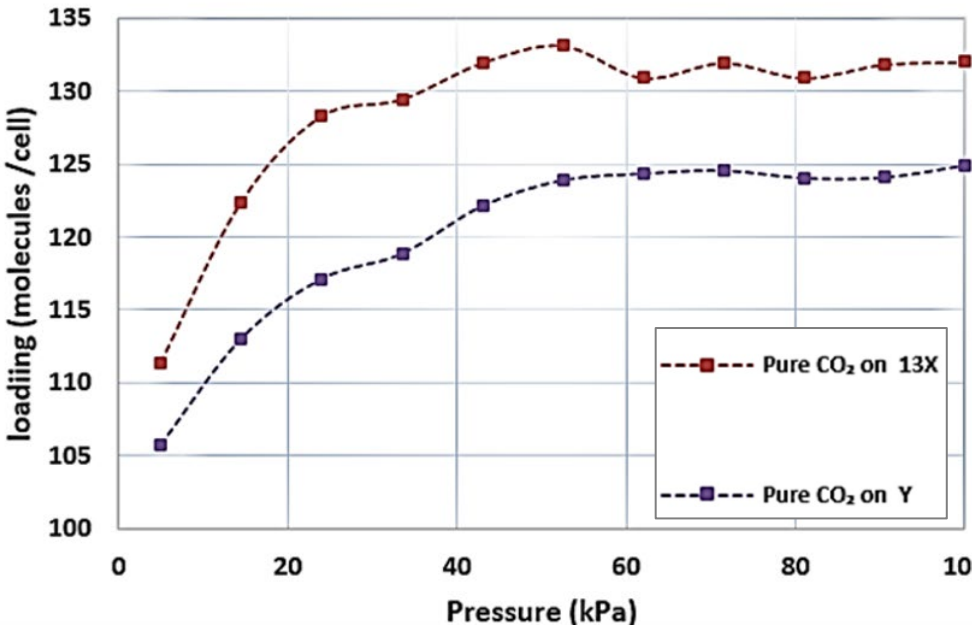

Figure 2. Pure CO_2 loading vs pressure for 13X and Y.

rather stable values for CO_2 at 54-56 molecules per cell even at 100 kPa. The lower cation density makes it harder for the water to saturate the pores. These results indicate that increasing the Si/Al ratio suppresses competitive H_2O adsorption and prevents the CO_2 roll-over effect under humid conditions [9,16].

3.3. Selectivity and Water Competition

As shown in Table 2, due to the higher value of Si/Al ratio in the case of Zeolite Y, fewer strong cationic adsorption sites in it, which leads to reduced interaction with water and reduces water accumulation in the pores. This reduced water affinity with increasing Si/Al ratio is consistent with previous studies on the relationship between zeolite composition, hydrophobicity, and water adsorption [18]. Despite the slightly lower capacity of CO_2 in comparison with 13X, Zeolite Y shows higher stability in humid conditions. Furthermore, the selectivity of zeolites towards CO_2 over H_2O was studied. Here, selectivity refers to the ratio of the loading of CO_2 to H_2O at equal pressures:

$$S_{CO_2/H_2O} = CO_2\ loading\ /\ H_2O\ loading \quad (2)$$

The selectivity values of both zeolites for the studied pressure range are presented in Table 2. These results indicate that increasing the Si/Al ratio improves the stability of CO_2 adsorption under humid conditions despite a slight reduction in selectivity.

Zeolite 13X shows slightly greater selectivity (0.74) at the lower pressure of 10 kPa compared with Zeolite Y (0.67). As the pressure increases, selectivity becomes smaller for both adsorbents because of increased water adsorption in the pores. However, it should be noted that although at the beginning selectivity is lower for the zeolite Y, it changes gradually during the increase of pressure. The most important thing is that Zeolite Y allows CO_2 to be adsorbed at a strong water competition. Thus, in a process with pressure variations, Zeolite Y should show more predictable behavior. This trend is consistent with previous experimental and simulation studies on high-silica FAU zeolites under humid conditions [9,10].

Table 2. CO_2/H_2O selectivity as a function of total pressure at 298 K.

Pressure (kPa)	Selectivity (Zeolite 13X)	Selectivity (Zeolite Y)
10	0.74	0.67
19	0.64	0.57
28	0.59	0.55
37	0.54	0.53
46	0.54	0.53
55	0.54	0.51
64	0.54	0.51
73	0.52	0.46
82	0.50	0.47
91	0.49	0.44
100	0.48	0.43

3.4. Isosteric Heats of Adsorption

Figure 4 demonstrates the averaged isosteric heats Q_s for CO_2 and H_2O. The use of isosteric heat as an indicator of adsorbate–adsorbent interaction strength is consistent with previous experimental and molecular-simulation studies of

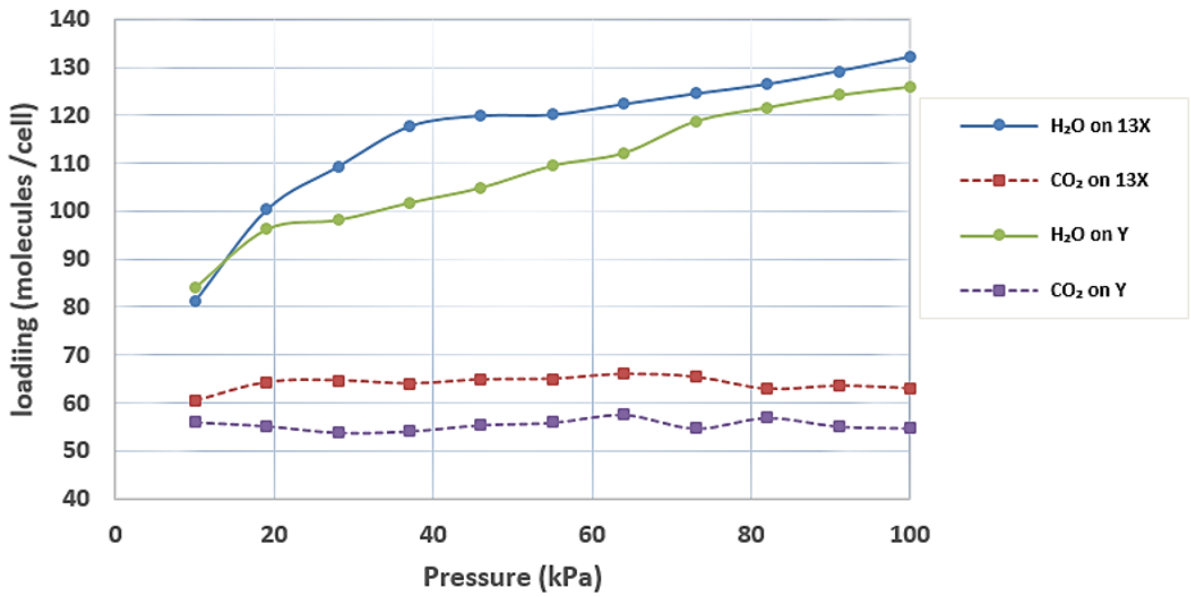

Figure 3. Loading vs pressure: four curves (H_2O/CO_2 on 13X/Y).

gases in zeolites [19]. As can be seen, isosteric heats of CO_2 decrease from 15.71 kcal/mol (13X) to 13.23 kcal/mol (Y). This means that regeneraion of Zeolite Y will need less energy than in case of 13X zeolite. These results indicate that Zeolite Y requires less regeneration energy than Zeolite 13X, making it more suitable for cyclic CO_2 capture under humid conditions.

In Table 3, there is a comparison of the isosteric heat of adsorption for pure CO_2 at zero coverage, calculated in this work using the GCMC method for equimolar mixture, and the same for pure CO_2 at zero coverage obtained experimentally by Lemecho *et al.* [9]. It should be noted that the difference between those is due to the fact that the experimental results were obtained for zero coverage with pure gas, while in our case the calculations are performed for the mixture. Nevertheless, the same qualitative trend is observed; 13X binds CO_2 more effectively than Y. These findings demonstrate that competitive adsorption under humid conditions substantially modifies the adsorption energetics compared with dry-gas measurements.

It is necessary to take a closer look into the discrepancy between the Q_{st} values we obtained and those provided by Lemecho *et al.* [9]. These values were found for pure CO_2 at zero coverage, which means an almost CO_2-free atmosphere where intermolecular forces can be neglected. On the contrary, in our research, an equimolar CO_2/H_2O mixture was studied, where CO_2 and water compete for the same adsorption sites. As was mentioned above, competitive adsorption in Zeolite Y results in lower heat of adsorption due to the preference of water molecules to occupy the most effective sites. In any case, the values we obtained cannot be numerically compared, although they give a more realistic representation of adsorption processes in humid streams.

The data on the decrease of the CO_2 binding energy due to the presence of water is shown in Table 4. The variable ΔQ is calculated as $\Delta Q = Q_{st,pure} - Q_{st,mixture}$. The value of the drop is significantly higher in the case of Zeolite Y (ΔQ = 2.03 kcal/mol) as compared to that for 13X (ΔQ = 1.14 kcal/mol), which this behavior can be

Table 3. Comparison of the isosteric heat of adsorption for CO_2 (kcal/mol).

Zeolite	This work (GCMC,mixture-averaged) (kcal/mol)	Lemecho *et al.* (pure CO_2, zero coverage) (kcal/mol)
13X (Na_{77}, Si/Al≈1.5)	15.71	≈16.44 (≈68.8 kJ/mol)
Y (Na_{49}, Si/Al≈2.92)	13.23	≈7.84 (≈32.8 kJ/mol)

Table 4. Reduction in average CO_2 binding energy (ΔQ) between pure-gas and mixture simulations at 100 kPa and 298 K.

Zeolite	$Q_{st,pure}$ (kcal/mol)	$Q_{st,mixture}$ (kcal/mol)	ΔQ (kcal/mol)
13X	16.85	15.71	1.14
Y	15.26	13.23	2.03

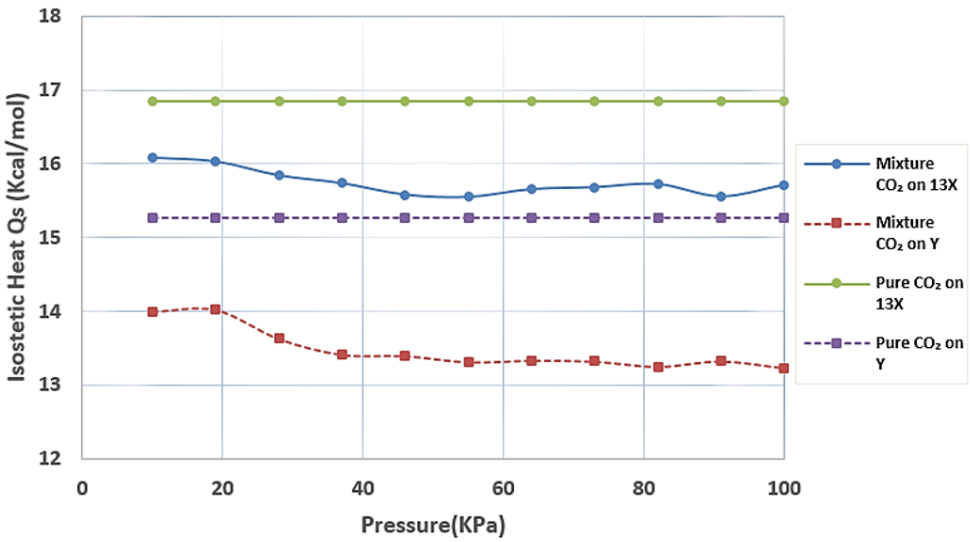

Figure 4. Q_{st} vs pressure for CO_2 and H_2O on both zeolites.

attributed to the reduced cation content in Zeolite Y; hence, water molecules occupy a significant portion of strong adsorption centers.

Practical implications of these results can be outlined as follows. The zeolite 13X exhibits better CO_2 uptake in the conditions of low and moderate pressures in the absence of moisture. Nevertheless, in case moisture is present, especially under fluctuating pressure, it reduces the stability of CO_2 adsorption thus making it unsuitable for application in the pressure swing adsorption process. On the other hand, Zeolite Y exhibits about 13% decrease in the capacity of CO_2 absorption but shows stable behavior under the whole range of pressures even in wet conditions. Although there is penetration of water into the zeolite pores, there is no rapid desorption of CO_2 molecules. Besides, lower isosteric heat of adsorption of CO_2 on zeolite Y (13.23 compared to 15.71 kcal/mol) implies lower energy costs for the process of thermal regeneration [9,17]. Thus, in case of using moist feed gas and variable pressures, Zeolite Y is preferable.

3.5. Limitations of the Simulations

We must be conscious of the limitations of our model with regards to its range of applicability. In the case of the existing GCMC approach, we have assumed a fixed structure of the zeolite framework as well as fixed positions of the cations. Although it is enough to describe the trends observed, there is some flexibility and the cations can also migrate with the addition of water molecules. Furthermore, in the calculation of Q_{st} using the fluctuation approach, one might obtain some weird results such as negative numbers for low loadings. This happens because of the strong competition conditions prevailing.

4. Conclusions

This study demonstrates that increasing the Si/Al ratio fundamentally changes the competitive CO_2/H_2O adsorption behavior in FAU zeolites under humid conditions. The GCMC simulations performed in our work explore how a decrease in the concentration of Na^+ ions in FAU zeolites due to a change in the zeolite composition from 13X to Y affects the competitive behavior of CO_2 and H_2O. An increase in the Si/Al ratio leads to a decrease in cation concentration, and hence in the ability of the framework to interact with water molecules - it is not sufficient to make the material hydrophobic but prevents complete adsorption of water in the pores. As a result, the adsorption of CO_2 in Zeolite Y does not experience any rollover effect at all, remaining practically unchanged during the entire range of pressures. Mixture-averaged Q_{ST} value for CO_2 decreases from 15.71 kcal/mol in 13X to 13.23 kcal/mol in Y, thus explaining why the regeneration energy in Y is lower. Binding energy loss for water-induced desorption (ΔQ) for Zeolite Y (2.03 kcal/mol) is larger than for 13X (1.14 kcal/mol). Practically, high-silica FAU zeolites with Si/Al ratio equal or larger than 2.9 are interesting for CO_2 capture from humid flue gas because of their more favorable regeneration energy. Thus, about a 13% loss in absolute CO_2 capacity compared with 13X offers significantly better cycling stability of this material.

Framework flexibility and mobilization of cations due to water clusters formation were neglected in our simulations. Nevertheless, these two factors should be included into the model since real zeolites have framework flexibility, and water clusters can move cations in the zeolite. Therefore, the following step includes performing Molecular Dynamics simulations with flexible framework and mobile cations. From experimental side, it is interesting to measure competitive breakthrough curves for CO_2/H_2O mixtures using NaY zeolite with precisely controlled Si/Al ratio and assess cycling stability under humid conditions. We continue expanding these simulations to other types of cations (e.g. Ca^{2+}, Mg^{2+}).

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CRedit Authors Statement

Author Contributions: Mustafa Jassim Radhi: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Writing – original draft, Writing – review & editing. All authors have read and agreed to the published version of the manuscript.

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