Adsorption Kinetics of CO₂, O₂, N₂, and CH₄ in Cation-Exchanged Clinoptilolite

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The rate of adsorption of pure CO₂, O₂, N₂, and CH₄ on natural untreated clinoptilolite-rich volcanic tuff (Cp) from Tehuacan (Puebla, Mexico), and on cation-exchanged clinoptilolite samples (Ca–Cp, K–Cp, and Na–Cp) has been measured at 20 °C using a glass high-vacuum volumetric apparatus. The X-ray diffraction pattern of Cp showed that the main crystalline phases correspond to clinoptilolite–heulandite and minor amounts of mordenite, cristobalite, feldspar (albite), quartz, smectite, and opal. The adsorption rates of gases in the initial period (t < 180 s) were measured with a custom acquisition data card capable of registering pressure and time data five times per second, simultaneously. The influence of cation exchange on adsorption kinetics of the gases depended on the gas-adsorbent contact time (t). In the initial period, the adsorption rate of all gases on all samples decreased in the order Ca–Cp > K–Cp > Cp > Na–Cp, and the affinity decreased in the order CO₂ > Na–Cp > O₂ > CH₄, whereas at equilibrium (t → ∞) the adsorption uptake decreased in the sequence CO₂ > CH₄ > N₂ > O₂. The slow adsorption of methane in Na–Cp was probably due to diffusional difficulties as a result of channel blockage by Na⁺ cations. By cation exchange of Cp an adsorbent can be tailored for the separation of N₂/O₂, N₂/CH₄, and CO₂/CH₄ mixtures.

Introduction

Zeolites are porous, crystalline, hydrated aluminosilicates of alkali and alkaline earth cations that possess a three-dimensional structure. The zeolite framework consists of an assemblage of SiO₄ and AlO₄ tetrahedra joined together in various regular arrangements through shared oxygen atoms to form an open crystal structure containing pores of molecular dimensions into which guest molecules can penetrate. The negative charge created by the substitution of an AlO₄ tetrahedron for a SiO₄ tetrahedron is balanced by exchangeable cations (e.g., Na⁺, K⁺, Ca²⁺, Mg²⁺), which are located in large structural channels and cavities throughout the structure. These cations play a very important role in determining the adsorption and gas-separation properties of zeolites. These properties depend heavily on the size, charge density, and distribution of cations in the porous structure. Synthetic zeolites are manufactured on a large scale for industrial use, but natural zeolites have not yet found extensive application as commercial molecular sieves, even though a few, particularly clinoptilolite, are abundant in volcanicogenic sedimentary rocks.† Of the more than 40 natural zeolites species known today, clinoptilolite is the most abundant in soils and sediments. The framework of clinoptilolite is formed by two parallel channels of 10-member rings (channel A) and eight-member rings (channel B) connected to a third channel C of eight-member rings.† The approximate channel sizes (Å) are: A, 4.4 × 7.2; B, 4.1 × 4.7; C, 4.0 × 5.5. Small hydrated cations (Na⁺, K⁺, Ca²⁺, and Mg²⁺) can easily enter the channels of clinoptilolite and compete for the major exchangeable-cation sites,‡ designated as M(1), M(2), M(3), and M(4). The major cations are located and distributed as follows:§ M(1) is located in channel A, where Na > Ca; M(2) is located in channel B, where Ca > Na; M(3) is located in channel C, where there is only K; and M(4) is located in channel A, where there is only Mg. Clinoptilolite has been applied to gas and radioactive wastewater cleaning, gas separation, and gas drying, and Minato et al. and Galabova et al. discussed the possibility of using clinoptilolites to separate oxygen from air. Others have shown that the use of K-exchanged clinoptilolite for air separation leads to an increase in the coefficient of oxygen production. Frankiewicz and Donnelly found that clinoptilolite can be used to separate N₂/CH₄ mixtures, and that an incompletely exchanged sample containing divalent cations appeared to be the most selective for N₂. Through cation manipulation, Ackley et al. tailored clinoptilolite for a commercially viable, kinetic separation of a N₂/CH₄ mixture. The affinity of zeolites for N₂ is attributable to the field gradient—quadrupole interaction energy, which is stronger for divalent cations than for monovalent cations. Boniface et al. reported that clinoptilolite appeared to be a promising adsorbent for O₂/Ar separation, but because O₂ is preferentially adsorbed, this adsorbent was not ideal for purifying oxygen. Mumpson noted that natural zeolites, primarily chabazite and clinoptilolite, have been used to purify natural gas contaminated with large amounts of CO₂, H₂S, and H₂O.

In view of the fact that large deposits of zeolitic tuffs,
primarily of clinoptilolite, have been discovered in Mexico, we began an investigation of the adsorption properties of these materials to evaluate their possible industrial applications, e.g., in gas separation processes. The particular objective of this study was to investigate the influence of cation exchange of natural clinoptilolite (Cp) (using aqueous solutions of salts NaCl, KCl, and CaCl2) on the adsorption kinetics of CO2, O2, N2, and CH4 at 20 °C.

Experimental Section

To simplify the notation, the untreated clinoptilolite-rich volcanic tuff is referred to below as Cp; Na−Cp, K−Cp, and Ca−Cp denote the cation-exchanged clinoptilolite samples.

Characterization of Samples. Methods. The X-ray powder diffraction (XRD) pattern of Cp was obtained on a Siemens D-5000 diffractometer using CuKα radiation (λ = 1.5406 Å), a step size of 0.02° 2θ and a counting time of 4.0 s/step. The XRD pattern showed (Figure 1) that the main crystalline phases correspond to a clinoptilolite-heulandite mineral17 and lesser amounts of mordenite, cristobalite, feldspar (albite), quartz, smectite, and opal. The chemical composition (Table 1) of the samples was obtained by means of a standardless method

Voyager 2100 and an energy-dispersive X-ray spectrometer (Voyager-Noran), coupled to a scanning electron microscope (JEOL-JSM-5400 LV). To obtain a more representative chemical composition of the sample bulk, the analysis was done on 10 different grains of each sample, and the element contents were averaged (Table 1). These data show that the Cp sample exhibits cation selectivity; e.g., Na+ was fully replaced by Ca2+, Ca2+ and K+ were only partially replaced by Na+, and Ca2+ was entirely replaced by K+.

The samples were also characterized by the classical N2-adsorption method at 77 K and water adsorption at 20 °C (Figure 2) in a glass high-vacuum volumetric system. The low adsorption of N2 at 77 K and the nearly negligible adsorption of water at 20 °C (Figure 2) on Cp and the exchanged samples (Ca−

<table>
<thead>
<tr>
<th>TABLE 1: Chemical Composition (weight %) of Untreated and Cation-Exchanged Clinoptilolite-Rich Tuff from Tehuacan, Puebla (Mexico)</th>
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</thead>
<tbody>
<tr>
<td>sample</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>Cp</td>
</tr>
<tr>
<td>Na−Cp</td>
</tr>
<tr>
<td>K−Cp</td>
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<tr>
<td>Ca−Cp</td>
</tr>
</tbody>
</table>

a Cp denotes the natural untreated clinoptilolite-rich volcanic tuff. The Na−Cp, K−Cp, and Ca−Cp samples were prepared by aqueous exchange of the Cp sample with sodium, potassium, and calcium chloride solutions, respectively.

Figure 1. X-ray powder diffraction pattern of Cp sample. C, Clinoptilolite; H, Heulandite; A, Albite (feldspar); Cris, Cristobalite; M, Mordenite; Q, Quartz; ss, sample support.

Figure 2. Adsorption isotherms of H2O (20 °C) and N2 (77 K). ■ Ca−Cp, ○ Cp, ▲ K−Cp, ◆ Na−Cp.
TABLE 2: Surface area (S) and Micropore Volume (Vp) of Untreated and Cation-Exchanged Clinoptilolite-Rich Tuff from Tehuacan, Puebla (Mexico)

<table>
<thead>
<tr>
<th>sample</th>
<th>S (m²/g)</th>
<th>Vp (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp</td>
<td>25</td>
<td>0.0506</td>
</tr>
<tr>
<td>Na–Cp</td>
<td>18</td>
<td>0.0480</td>
</tr>
<tr>
<td>K–Cp</td>
<td>17</td>
<td>0.0500</td>
</tr>
<tr>
<td>Ca–Cp</td>
<td>25</td>
<td>0.0650</td>
</tr>
</tbody>
</table>

- H₂O adsorption, Dubinin-Astakhov (n = 1). Sample abbreviations are as in Table 1.

Cp, K–Cp, Na–Cp) was probably due to kinetic effects, i.e., at 77 K nitrogen molecules diffused into micropores with considerable difficulty and even after more than 8 h did not attain adsorption equilibrium. The samples gave type-IV N₂-adsorption isotherms, and the BET model described the experimental points up to P/P₀ ≤ 0.40 perfectly. The Langmuir model was able to fit the adsorption isotherms only over the range 0.01 ≤ P/P₀ ≤ 0.10. Unlike the N₂ adsorption isotherms, H₂O adsorption isotherms were of type I; thus, the molecules of H₂O were able to penetrate freely into the micropores. The micropore volume (Dubinin-Astakhov) of samples decreased in the order: Ca–Cp > Cp ≈ K–Cp > Na–Cp (Table 2).

Ion Exchange. The Na–Cp, K–Cp, and Ca–Cp samples were prepared by aqueous exchange of Cp with sodium, potassium, and calcium chloride solutions at 0.5 N concentration. Before each cation-exchange treatment, the Cp was washed with distilled water to eliminate soluble impurities. One gram (fraction 20–30 mesh) of Cp was placed in a 1.4-cm diameter glass ion-exchange column of 12-cm length and held at 65 °C. Subsequently, 200 mL of solution was percolated through the samples for 30 min. This cation-exchange procedure was repeated twice. After the cation-exchange treatment the samples were thoroughly washed with distilled water until the filtrate was free of chloride ions. To evaluate the success of the cation-exchange process, the exchange treatment was repeated. After four additional cation-exchange treatments, the Na content increased by only 1.8% absolute.

Adsorption Kinetics Measurement. The adsorption of CO₂, O₂, N₂, and CH₄ as a function of time t was obtained by the volumetric method on the basis of the difference between the initial amount of gas introduced into the cell and the amount of gas remaining in the dead space of the cell at any given time t, from t = 0 until t = ∞ (equilibrium). In all experiments, the initial pressure was 450 Torr (600 mb). The high-vacuum system was made of Pyrex glass, which was equipped with grease-free valves and calibrated with He. The vacuum was created by a turbomolecular pump (TSH 062, Balzers) capable of establishing pressures as low as 10⁻¹⁰ Torr. The pressures were measured by two types of pressure transducers (Balzers) of different range: TPR 017 (10⁻⁴–5 Torr) and APR 011 (1–1000 Torr). About 500 mg of each sample were first dehydrated in situ at 280–320 °C in an oven up to a residual pressure of < 6 × 10⁻⁴ Torr. After sample dehydration, the temperature was decreased to the desired point at which time the sample was allowed to stabilize for at least 1.5 h before the beginning of the measurement. To analyze in detail the sudden drop in pressure that occurred when the gases were put into contact with the adsorbents, a custom acquisition data card was used which allows simultaneous monitoring and recording of time and pressure. In the period 0–3 min, pressure was monitored five times per second because this initial period is the most important period in gas separation processes, such as the pressure swing adsorption method (PSA). Afterward, in the period 3–13 min, pressure was registered once per second, and pressure was recorded once every 10 seconds in the period 13–∞ min.

The size and polarizing power of the cations present in the zeolite channels may influence the selective adsorption of certain molecules, and the adsorptive properties of a heteroionic natural zeolite that is converted to a near homionic form, should therefore change. In the next section the adsorption uptake curves of each gas are shown separately. From differences in adsorption kinetic behavior of the gases, we propose what appears to be the best sample for the separation of certain binary gas mixtures.

Results

Adsorption Kinetics of Pure Gases. Figures 3, 4, 5, and 6 show the adsorption uptake of N₂, O₂, CH₄, and CO₂, respectively, both for short (t ≤ 100 s) (a) and long (t → ∞) (b) gas-adsorbent contact times. These figures show the marked influence of cation type on the adsorption uptake of all gases, especially for short contact times. To evaluate the effect of cation-exchange, the adsorption uptake by the untreated sample (Cp) is also included in these figures. In the initial uptake region (t ≤ 100 s), the adsorption rate decreased in the following order Ca–Cp > K–Cp > Cp > Na–Cp. For the Cp and K–Cp samples, the uptake curves (see Figures 4a, and 6a) of O₂ and CO₂ were very similar. At equilibrium, however, the adsorption rate of these gases in the initial uptake region (t < 100 s) on all samples,
and for the Cp and Na–Cp samples for $t \rightarrow \infty$, decreased in the order CO$_2$ ≫ N$_2$ > O$_2$ > CH$_4$. However, the adsorption uptake for $t \rightarrow \infty$ behaved in the following way for Ca–Cp:

$\text{CO}_2$ > $\text{CH}_4$ > $\text{N}_2$ > $\text{O}_2$. The fact that for Cp and Na–Cp samples, which contain Na$^+$ cations (Table 1), the adsorption uptake decreased in the order CO$_2$ ≫ N$_2$ > O$_2$ > CH$_4$ both for short and long gas–adsorbent contact times, suggests that the Na$^+$ cations occupied positions in the zeolite structure that caused diffusional restrictions to the larger CH$_4$ molecule. CO$_2$ had the highest affinity of the adsorbates studied in all clinoptilolite samples because of strong ion–quadrupole interactions.

**Adsorption Kinetics of Gas Pairs.** (a) **N$_2$/O$_2$.** Figure 7 compares the adsorption kinetic behavior of N$_2$ and O$_2$ in different cation-exchanged samples with the corresponding kinetic behavior of the Cp sample. Interestingly, the adsorption uptake of O$_2$ on Cp in the region $t \leq 20$ s was close to that of N$_2$ (Figure 7a). For the Na–Cp sample, this effect was the same until $t \leq 120$ s. Furthermore, the adsorption uptake of both gases by this sample was lower than by Cp. Unlike the results for the Na–Cp sample, the amounts of both gases adsorbed by the K–Cp and Ca–Cp samples were greater than for Cp, especially for the Ca–Cp sample. The uptake of N$_2$ was greater than that of O$_2$ in all samples, due to the higher quadrupole moment of N$_2$ compared with that of O$_2$. The difference in the adsorption uptake suggests that the Ca–Cp and K–Cp samples could be used for O$_2$ enrichment from air. By virtue of the greater difference between the uptake curves of N$_2$ and O$_2$ for Ca–Cp, compared with K–Cp, Ca–Cp would probably be the best material for O$_2$ enrichment from air.

(b) **N$_2$/CH$_4$.** Figure 8 shows that samples Ca–Cp, K–Cp, and Cp were highly selective for N$_2$ over CH$_4$. The selectivity for N$_2$ decreased in the order Ca–Cp > K–Cp > Cp ≫ Na–Cp, i.e., the Ca–Cp sample seemed to be the most suitable for the separation of this gas mixture. However, because CH$_4$ adsorption on K–Cp and Ca–Cp samples increased slowly with
time, reaching the $N_2$ adsorption of $Ca^{2+}$ and exceeding the $N_2$ adsorption of $K^+$ at equilibrium, these samples are not recommended for purifying $N_2$ contaminated with $CH_4$, at long gas-contact times. These results coincide with those reported by other authors$^{13}$ for $K^+\text{-}\text{clinoptilolite}$. $CH_4$ adsorption on these samples was probably determined by diffusive restrictions in micropores, principally in the $Na^-$ sample. Therefore, the adsorptive separation of this gas mixture can be achieved by virtue of differences in diffusion rates of these molecules.$^{21}$

(c) $CO_2/CH_4$. As indicated above, $CO_2$ had the highest affinity in all samples, a fact that is attributable to the specific interactions of the $CO_2$ quadrupole with the electric field created by the cations in the zeolite structure. Thus, if the $CO_2/CH_4$, $CO_2/O_2$, and $CO_2/N_2$ mixtures were contacted with any of the four studied clinoptilolite samples, $CO_2$ would be adsorbed preferentially, leading to a purification of these gases. Figure 9 shows that for short contact times ($t < 100$ s), $Ca^{2+}$ would be the most effective of the lot for separation of the $CO_2/CH_4$ mixture, whereas at equilibrium the $Na^-$ sample would have the highest efficiency, because the $CH_4$ adsorption in this sample was negligible.

**Discussion**

To interpret the results, the chemical composition (Table 1) and crystal structure of the adsorbents must be considered, as well as the fundamental properties of the exchanged cations$^{22-24}$ (Table 3) and the adsorbate molecules$^{25}$ (Table 4). Chemical analyses reveal that untreated $Cp$ was rich in alkali ($Na$, $K$) and poor in alkaline-earth metals ($Ca$, $Mg$). The most noticeable feature of the cation-exchange process was the high selectivity of clinoptilolite for $K^+\text{ cations}$, which is in accord with the results of other authors$^{3,11,26}$. The uptake rate of the gases in the initial region ($t \leq 100$ s), decreasing in the order $Ca^{2+}>K^->Cp>Na^-$, correlates with the $Ca^{2+}$ and $Na^+$ contents in the zeolitic channels, and the highest adsorption rate
occurred for a zeolite that had more Ca\(^{2+}\) and less Na\(^{+}\). The fact that the uptake curve for Cp was situated above the Na–Cp curve may be due to the higher Ca\(^{2+}\)– and lower Na\(^{+}\) content of the untreated Cp compared with Na–Cp (Table 1).

To evaluate the adsorption rate of each gas, the time required to occupy half of the total adsorption capacity \((n_a)\) was evaluated. This time \((t_{1/2})\) corresponds to the relationship \(n_t/n_a = 0.5\), where \(n_t\) and \(n_a\) are the uptake at time \(t\) and \(t_a\) (equilibrium), respectively. The values of \(t_{1/2}\) (Table 5) show that CH\(_4\), with the largest kinetic diameter (Table 4), is adsorbed more slowly than the other gases, perhaps due to diffusive restrictions in the zeolite channels. Apparently, the instantaneous adsorption of CH\(_4\) on the Na–Cp sample (Table 5) was due to the inability of the CH\(_4\) molecule to enter the zeolite channels and, consequently, this gas was adsorbed only on the external surface of the Na–Cp sample. This supposition is supported by the fact that for this sample, the values of \(t_{1/2}\) for the other three gases increased in the sequence CO\(_2\) < O\(_2\) < N\(_2\) (Table 5), in order of the increasing size of these molecules (Table 4). Given the \(t_{1/2}\) value of 16 s for Na–Cp with CO\(_2\), which has the lowest kinetic diameter of the gases studied, it is likely that the very low value of \(t_{1/2}\) (<1 s) measured for the CH\(_4\) molecule suggests that in fact the micropores did not take part in the adsorption of CH\(_4\) on this sample. From the CH\(_4\) adsorption uptake behavior at 0 °C and 20 °C, the \(t_{1/2}\) value apparently did not depend on temperature and, therefore, the activation energy \((E_a)\) was equal to zero. This means that the adsorption of CH\(_4\) in this temperature range (0–20 °C) was not controlled by a diffusion process. Likewise, for the other three samples, a diffusion process did not control CH\(_4\) adsorption.

Figure 10 compares the adsorption uptake behavior of N\(_2\) and CH\(_4\) on the Ca–Cp and K–Cp samples. Note that the time required to reach total CH\(_4\) uptake \((n_a)\) for these samples was about 5 h. Note also that the \(n_a\) value for CH\(_4\) reached and overcomes \(n_a\) for N\(_2\) on the Ca–Cp and K–Cp samples, respectively. If the CH\(_4\) molecule enters the zeolite micropore structure freely, as in natural erionite,\(^{27}\) then the adsorption uptake of CH\(_4\), according to the polarizability of the gases, would be greater than for N\(_2\) at any gas-adSORBent contact times.

Accordingly, the fact that the N\(_2\) adsorption uptake on all samples was greater than for CH\(_4\) at short times, as well as for the Cp and Na–Cp samples at equilibrium, suggests that the location of cations in the channels of clinoptilolite plays a very important role. Moreover, from the fact that CH\(_4\) uptake reached and overcame N\(_2\) adsorption uptake for Ca–Cp and K–Cp, respectively, it can be supposed that the channel blockage factor decreased in the following order: Na >>> Ca > K. Thus, the lower gas adsorption, especially for CH\(_4\), shown for Na–Cp sample at low contact times, can be attributed to the reduction of effective channel aperture sizes by Na\(^{+}\) cations. This supposition is supported by the \(t_{1/2}\) values for CO\(_2\), O\(_2\), and N\(_2\) (Table 5) decreasing in the sequence Na–Cp > Cp, i.e., in order of the decreasing content of Na\(^{+}\) cations (Table 1), and by the fact that the \(\Delta t_{1/2} (s) = t_{1/2} (Na–Cp) - t_{1/2} (Cp)\) for each gas increased as follows: CO\(_2\) (10) < O\(_2\) (22) < N\(_2\) (357), i.e., in the order of the increasing kinetic diameters of molecules (Table 4). The similar adsorption uptake of N\(_2\) and O\(_2\) on the Na–Cp and Cp samples at low gas-adSORBent contact times (Figure 7a) could be due to the greater influence of channel blockage by the Na\(^{+}\) cations on the diffusion of N\(_2\).
which is larger than \( \text{O}_2 \). In contrast to the \( \text{CH}_4 \) adsorption kinetic behavior, \( \text{O}_2, \text{N}_2, \) and \( \text{CO}_2 \) adsorption occurred quickly on \( \text{K}^-\text{Cp} \) and \( \text{Ca}^{2+}\text{Cp} \) samples.

To understand the adsorption kinetic behavior of other gases, the \( \text{CO}_2 \) adsorption kinetic behavior was used as reference, inasmuch as this molecule is smaller and has the greatest polarizability and quadrupole moment in comparison with \( \text{N}_2, \text{O}_2, \) or \( \text{CH}_4 \). The \( \text{CO}_2 \) molecule is best suited\(^{28} \) as an acidic probe to characterize the basicity of the zeolites. Figure 6a shows that the basicity increased from \( \text{Na}^-\text{Cp} \) to \( \text{Ca}^{2+}\text{Cp} \). In other words, if \( \text{Na}^+ \) and \( \text{K}^+ \) were replaced by \( \text{Ca}^{2+} \), the basicity of the basic centers (i.e., framework oxygens) increased, which is consistent with the higher electronegativity of \( \text{Ca}^{2+} \) (Table 3). The sequence of increasing basic character \( \text{Na}^-\text{Cp} < \text{K}^-\text{Cp} < \text{Ca}^{2+}\text{Cp} \) at low gas-adsorbent contact times (Figure 6a) is somewhat puzzling because it is not consistent with other cation characteristics (electronegativity, ionic potential). However, for long gas-adsorbent contact times, as expected, the basic character increases in the order \( \text{K}^+ < \text{Na}^+ < \text{Ca}^{2+} \). Figures 3b, 4b, 5b, and 6b show that the time \( (t) \) required for the adsorption uptake of each gas on \( \text{Na}^-\text{Cp} \) to reach the adsorption uptake level on \( \text{K}^-\text{Cp} \) increased in the following order \( \text{CO}_2 (500) < \text{O}_2 (3000) < \text{N}_2 (8000) < \text{CH}_4 \) (never), correlating fairly well with the increasing order of kinetic diameter \( (\text{Å}) \) of molecules: \( \text{CO}_2 (3.3) < \text{O}_2 (3.46) < \text{N}_2 (3.64) < \text{CH}_4 (3.8) \). Obviously, the reduction of effective channel apertures by \( \text{Na}^+ \) cations greatly influenced the adsorption of \( \text{CH}_4 \).

**Summary**

The cation exchange of natural clinoptilolite-rich tuff (Cp) with \( \text{NaCl}, \text{KCl}, \) and \( \text{CaCl}_2 \) aqueous solutions substantially influenced the adsorption kinetics of \( \text{CO}_2, \text{O}_2, \text{N}_2, \) and \( \text{CH}_4 \). In the initial uptake region \( (t < 100 \text{ s}) \), the adsorption rate of all four gases on the studied samples decreased in the order: \( \text{Ca}^{2+}\text{Cp} > \text{K}^-\text{Cp} > \text{Cp} > \text{Na}^-\text{Cp} \). The adsorption uptake on all samples in the initial period \( (t < 100 \text{ s}) \), as well as for \( \text{Cp} \) and \( \text{Na}^-\text{Cp} \) at equilibrium \( (t \rightarrow \infty) \), decreased in the order \( \text{CO}_2 \gg \text{N}_2 > \text{O}_2 > \text{CH}_4 \). For \( \text{Ca}^{2+}\text{Cp} \) and \( \text{K}^-\text{Cp} \), however, the selectivity at equilibrium decreased in the sequences: \( \text{CO}_2 \gg \text{N}_2 \approx \text{CH}_4 > \text{O}_2 \) and \( \text{CO}_2 \gg \text{CH}_4 > \text{N}_2 > \text{O}_2 \), respectively. The slow adsorption of \( \text{CH}_4 \) was probably due to diffusive restrictions in zeolite channels, which was principally the result of channel blockage by \( \text{Na}^+ \) cations. The influence of this blockage on the adsorption rate decreased with decreasing kinetic diameter of the gas molecules.

Based upon the results of this study, cation exchange of \( \text{Cp} \) could possibly be tailored to produce an adsorbent for the separation of \( \text{N}_2/\text{O}_2, \text{N}_2/\text{CH}_4, \) and \( \text{CO}_2/\text{CH}_4 \) mixtures. All samples, including \( \text{Cp} \), can be applied in the separation of \( \text{CO}_2/\text{CH}_4 \) mixtures, but the \( \text{K}^-\text{Cp} \) and \( \text{Ca}^{2+}\text{Cp} \) samples will probably be the most effective for the separation of \( \text{N}_2/\text{O}_2 \) and \( \text{N}_2/\text{CH}_4 \) mixtures.