On the Structure–Property Relationships of Cation-Exchanged ZK-5 Zeolites for CO₂ Adsorption

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The CO₂ adsorption properties of cation-exchanged Li⁺, Na⁺, K⁺, and Mg-ZK-5 zeolites were correlated to the molecular structures determined by Rietveld refinements of synchrotron powder X-ray diffraction patterns. Li⁺, K⁺, and Na-ZK-5 all exhibited high isosteric heats of adsorption (Q_st) at low CO₂ coverage, with Na-ZK-5 having the highest Q_st (ca. 49 kJ mol⁻¹). Mg⁺⁺ was located at the center of the zeolite hexagonal prism with the cation inaccessible to CO₂, leading to a much lower Q_st (ca. 30 kJ mol⁻¹) and lower overall uptake capacity. Multiple CO₂ adsorption sites were identified at a given CO₂ loading amount for all four cation-exchanged ZK-5 adsorbents. Site A at the flat eight-membered ring windows and site B/B* in the γ-cages were the primary adsorption sites in Li⁺ and Na-ZK-5 zeolites. Relatively strong dual-cation adsorption sites contributed significantly to an enhanced electrostatic interaction for CO₂ in all ZK-5 samples. This interaction gives rise to a migration of Li⁺ and Mg⁺⁺ cations from their original locations at the center of the hexagonal prisms toward the α-cages, in which they interact more strongly with the adsorbed CO₂.

Introduction

CO₂ capture and storage (CCS) technology to reduce anthropogenic CO₂ emission has become one of the most urgent environmental issues in 21st century.[1] Adsorption is one of the most promising techniques for commercial and industrial CCS applications among proposed techniques such as cryogenic distillation,[2] membrane-based separation,[3] electrochemical sequestration in ionic liquid,[4] and chemical absorption with amine and ionic liquid solvents.[5] This is in part the result of the lower energy requirements, the ease with which materials can be processed, and a broad applicability over a relatively wide range of temperatures and pressures.[5] Porous adsorbents, including metal–organic framework (MOFs), activated carbon, and zeolites, were studied extensively for CCS because of their versatile structures, high porosity, and tunable adsorptive properties.[6–10] Recent efforts have correlated the relationship between structural characteristics and CO₂ adsorption properties to improve the performance of existent adsorbents and potentially design new adsorbent materials.[6–8] The adsorptive separation of CO₂ from other gases is based on both size and electronic properties of the gas molecules to be separated with consideration of the host framework. In terms of largest-scale separations needed (CO₂/N₂ and CO₂/CH₄), the small difference in kinetic diameters between CO₂ (3.30 Å), N₂ (3.64 Å), and CH₄ (3.80 Å) makes kinetic separation very challenging. However, microporous adsorbents with tailored narrow pore openings can selectively separate CO₂ from the molecules with larger kinetic diameter. For example, Liu et al. reported high selectivity of CO₂ over N₂ on zeolite NaKA owing to the exclusion of N₂ given its slightly larger effective kinetic diameter.[10] Palomino et al. proposed that the extremely high selectivity of CO₂/CH₄ on zeolite RHO is mainly a result of the pore aperture, which effectively blocks the adsorption of CH₄.[10] Lozinska et al.[11] studied the structure of Na⁺, K⁺, and Cs⁺-RHO zeolites and suggested that the cations in the intercage window sites effectively block CH₄ adsorption but relocate during the adsorption of CO₂ in a temperature-dependent “trapdoor” mechanism proposed by Webley and co-workers.[12]

In addition to a smaller size, CO₂ has a larger polarizability and quadrupole moment than N₂, which leads to stronger interactions of CO₂ with the electric field and electric field gradients within the adsorbents. The lack of a quadrupole moment for CH₄ is a key factor to be considered in designing adsorbents for CO₂/CH₄. CO₂ is a Lewis acid and has been used as a probe for elucidating the basic character of zeolites by IR spectroscopy and temperature programmed desorption.[13] The Lewis basicity of the adsorbents can also play an important role in determining adsorption properties under certain pressure regimes. Walton et al.[14] and Pingruber et al.[15] reported that the adsorption capacities at low pressure in faujasite zeolites are in the order Cs⁺ > K⁺ > Na⁺ > Li⁺ owing to the high basicity of the framework oxygen atoms, which is predominantly relative to the strength of the quadrupole interaction. Additionally, MOFs functionalized with basic nitrogen-containing organic groups were studied to improve the selectivity of CO₂.

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over N₂ and CH₄ owing to the strong acid–base interaction between the lone-pair of nitrogen and CO₂.[14]

The presence of uncoordinated metal sites in microporous MOF materials is significant for the high selectivity of CO₂ over other gases,[21,27,28] but these materials have been reported to be moisture-sensitive and chemically unstable, meaning that their practical use may be limited,[14] although there are exceptions.[20] MOFs without open metal sites, those potentially suitable in the humid environment of a flue gas, generally show higher CO₂ capacity at high pressures compared to zeolites owing to their high surface areas and porosities, but also relatively low CO₂ capacity at low partial pressures.[14a] Therefore, these materials might not be best suited to current post-combustion capture technologies given the low partial pressure of CO₂ in a low-pressure flue gas mixture or lower CO₂ selectivity under high-pressure conditions.[14] In contrast, although chemically robust and inexpensive, activated carbon has a lower uptake and selectivity at low pressures than zeolites, thus reducing its effectiveness as a potential CO₂ adsorbent.[15] Zeolites have good chemical and thermal stability, making them ideal industrial adsorbent materials. Zeolites are generally characterized by a relatively high CO₂ capacity and selectivity over other small gases at low pressure, which makes them promising candidates for CO₂ separation from flue gases.[14a,18b] The complex factors of exchanged cation types, acidity/basicity, and electrostatic interactions within zeolites help distinguish them from other types of adsorbents but can lead to very complex structure–property relationships in the adsorption for these materials. Furthermore, the high affinity for CO₂ in low-silica zeolites hinders desorption and can thereby have negative effects on regeneration and cost. The optimum Si/Al ratio for CO₂ adsorption/desorption cycles in LTA zeolites was found to be higher than Si/Al = 5,[20] with several studies showing the promise of small-pore, high-silica zeolites for CO₂ separations.[21] ZK-5 is one such zeolite that was shown to be a good candidate for CO₂ separation[22] in addition to being studied for adsorption and catalytic applications such as the selective synthesis of dimethylamine,[23] selective catalytic reduction,[24] and adsorption of hydrocarbons,[25] water, methanol, and acetonitrile.[26]

Zeolite ZK-5 (Zeolite Kerr with sequence number five) is a KFI-type framework first synthesized by Kerr in 1966.[27] The framework structure can be built from an alternating sequence of grc and pau units, the α– and γ-cages, respectively. Each α-cage is connected through flat eight-membered ring (8MR) faces to six γ-cages, and each γ-cage is connected to two α-cages and four other γ-cages. The largest α-cage in KFI has a free volume of approximately 707 Å³, which is smaller than the α-cage of LTA and RHO, which also contains a free volume of 264 Å³.[28,29] The nature and the distribution of the extra-framework cations in the cages of the framework play a crucial role in the adsorption properties of CO₂ in zeolite adsorbents.[14a,14b] Their presence not only induces modifications of the basicity and electrical field inside the pores, but it can also change the available pore volume and morphological structure of the zeolites, thereby influencing the adsorption kinetics. Here we report investigations of zeolite ZK-5 as a function of cation exchange (Li⁺, Na⁺, K⁺, and Mg²⁺) versus CO₂ adsorption using synchrotron powder X-ray diffraction (XPD) and CO₂ gas-adsorption isotherms measurements.[30] Excellent agreement between the cation locations and the adsorption sites is observed. Understanding the structure–property relationships between the dehydrated zeolite structure and that of the ZK-5 zeolite with adsorbed CO₂ can be the basis for designing and optimizing other adsorbents for CO₂ capture.

Results and Discussion

Initial ZK-5 characterization by gas adsorption

Surface areas were calculated by the Brunauer–Emmett–Teller (BET) method and micropore volumes were extracted using the t-plot method (Table S2 in the Supporting Information). The highest micropore volume amongst the four cation-exchanged ZK-5 zeolites was observed for Li-ZK-5. This larger volume may be the result of the smaller volume occupied by Li⁺ within the framework, but also of the stronger interaction between Li⁺ and N₂. Mg-ZK-5 showed a comparable micropore volume to that of Li-ZK-5 but a slightly lower micropore surface area owing, in part, to the weaker interaction with N₂. The lower specific surface areas and smaller pore volumes of Na-ZK-5 and K-ZK-5 are the result of the larger volume occupied by the heavier Na⁺ and K⁺ atoms in the α-cage of zeolite ZK-5. The placement of cations in the structure of the ZK-5 zeolites will be discussed in subsequent sections.

Adsorption isotherms up to 1 bar at 283, 303, 323, and 343 K were fit with both dual-site Langmuir (DSL) and dual-site Langmuir–Freundlich (DSLFI) equations leading to an accurate description of the adsorption in all four ZK-5 zeolites. Figure 1 shows the volumetric adsorption isotherms expressed in terms of molecules CO₂ per unit cell (uc) to allow for a more direct comparison between the samples as a function of pressure. The adsorption capacities of cation-exchanged ZK-5 zeolites at a given pressure all decreased with increased temperature, a behavior typical of physical adsorption. Additional adsorption isotherms in the more conventional mol/kg⁻¹ units are provided in the Supporting Information (Figures S2–S5, Tables S3–S4). At low pressures, there was a similar trend in the adsorption capacity per uc for Li-, Na-, and K-ZK-5 at each temperature. The overall capacity, up to a pressure of 1 bar, was greatest per uc in Li-ZK5, followed closely by Na-ZK-5. This trend from Li- and Na- to K-ZK-5 is, in part, explained by the increasing pore volume occupied by the exchanged cations, which reduces the volume available for adsorption of CO₂ when close to saturation. In the case of Mg²⁺, however, there exists evidently a weaker interaction with CO₂ that shifts the saturation pressure to higher values and provides a more gradual adsorption up to 1 bar pressure. These trends will be discussed further in the context of the CO₂-loaded powder diffraction structure refinements.

Figure 2 shows the isosteric heats of adsorption Qₑ as a function of loading for each of the four ZK-5 samples as calculated using the Clausius–Clapeyron equation from fitting the isotherm data (see the Supporting Information for more details.
and the $Q_{st}$ as a function of mmol$^{-1}$ in Figure S6), Initial $Q_{st}$ was greatest for Na-ZK-5 (ca. 49 kJ mol$^{-1}$), followed closely by Li-ZK-5 (ca. 45 kJ mol$^{-1}$), and K-ZK-5 (ca. 42 kJ mol$^{-1}$). Up to 12 CO$_2$ per uc, $Q_{st}$ remained highest in Na$^+$, followed by Li$^+$ and K$^+$ as reflected by the steepness of the initial parts of the isotherms. $Q_{st}$ decreased quickly for Na-ZK-5 and somewhat less quickly for Li-ZK-5 beyond this loading, whereas the adsorption heats for K-ZK-5 even increased slightly with more adsorbed CO$_2$. Interestingly, Mg$^{2+}$ with less than half of the cation population showed much lower adsorption heats than the other cations.

Overall, the adsorption capacities and isosteric heats of adsorption determined in this study were similar to those observed in higher-silica ($Si/Al = 4.75$) ZK-5. At room temperature and pressure (ca. 303 K and 1 bar), Li-ZK-5 showed similar adsorption capacity to Li- and Na-SSZ-13 ($Si/Al = 6$), NaY, NaX (ca. 5 mmol g$^{-1}$) and a much higher adsorption capacity than that of other zeolites with higher framework densities such as FER, STI, MFI, MEL, or TUN (ca. 5 mmol g$^{-1}$). Owing to the higher micropore volume of SSZ-13 (ca. 0.27 cm$^3$ g$^{-1}$), the slopes of CO$_2$ adsorption isotherms above atmospheric pressure for Na-, Li-SSZ-13/6, NaY, and Na13X materials are higher than those of Li- and Na-ZK-5, indicating that their saturation capacities are higher than those of the cation-exchanged ZK-5 adsorbents (Figures S2–S5). The adsorption heats of Na-ZK-5 near zero coverage were close to low-silica faujasite Na13X, higher than Li- and Na-SSZ-13/6, and much higher than NaY, even though Na-ZK-5 has much lower cation concentration than low-silica.
faujasites. This indicates a strong interaction between adsorbed \( \text{CO}_2 \) molecules and the KFI framework or \( \text{Na}^+ \) cations located in the ZK-5 zeolite.

**Structure of dehydrated cation-exchanged ZK-5 zeolites**

Elucidation of the extra-framework cation locations in cation-exchanged ZK-5 is necessary to fully understand the structure–property relationship of \( \text{CO}_2 \) adsorption. The dehydrated ZK-5 structures were refined in a body-centered cubic space group \( \text{Im}3\text{m} \) with a unit cell containing 96 symmetry-equivalent tetrahedral Si or Al atoms and 192 oxygen atoms. One unit cell consists of two \( \alpha \)-cages and six \( \gamma \)-cages (Figures S7 and S8). Four cation sites (\( \text{SI, SI}', \text{SIi, and SIII} \)) were determined in zeolite ZK-5 and are shown in Figure 3. Site I is found in the center of the hexagonal prism in which cations have octahedral coordination with the neighboring framework oxygen atoms. Site I' is located at the edge of the \( \alpha \)-cage close to the hexagonal window of the hexagonal prism, and each cation coordinates to three oxygen atoms. Site II is located in the center of the “puckered” 8MR. Site III settles in the flat 8MR in which each cation is coordinated to the four nearest framework oxygen atoms. The refined unit-cell parameters, cation locations, occupancies, and other key values determined for dehydrated, cation-exchanged Mg-, Li-, Na-, and K-ZK-5 are reported in Table 1.

The locations of the cations in the exchanged ZK-5 zeolites, as determined from XPD, are illustrated in Figure 4 for all four samples. The refined cation compositions for all samples agree well with the results from inductively coupled plasma (ICP) and energy-dispersive X-ray spectroscopy (EDX) methods (Table S1). For Li-ZK-5, the refined model has slightly lower Li\(^+\) content than the value determined from ICP (by 4%). This may be in part owing to the fact that the remaining Li\(^+\) is occupying other disordered sites at very low occupation, and as such, it is likely too weak a scatter to be observed in XPD. The presence of residual K\(^+\) in Li-ZK-5 was observed by X-ray fluorescence (XRF): It is located in the middle of the puckered 8MRs from XPD refinement. Li\(^+\) is observed solely at position SI' because this coordination environment is, as expected, the most favorable for a small cation. This was also observed in faujasite and chabazite zeolites.\(^{31,33}\) Li\(^+\) is displaced out of the plane of a six-membered ring (6MR) and the three closest framework oxygen atoms.

![Figure 3](image-url)  
**Figure 3.** Illustration of the KFI structure (Si/Al (blue), O (red)) and typical cation (grey spheres) locations in the zeolite pores.

![Figure 4](image-url)  
**Figure 4.** Left: Cation sites in the hexagonal prism: Li\(^+\) (site I' cyan), K\(^+\) (site I' purple), Na\(^+\) (site I, I' orange). Right: Na\(^+\) (orange) shown in the puckered 8MRs and K\(^+\) (purple) in the flat 8MRs. The dashed lines indicate the closest cation-framework oxygen (red) contacts in ZK-5.

### Table 1. 
Refined unit-cell parameters, cation locations, occupancies, and closest cation-framework oxygen distances in cation-exchanged ZK-5. Values in parentheses indicate one standard deviation in the final digit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unit cell ( a [\text{\AA}] )</th>
<th>Site I occup.</th>
<th>( d_{\text{M-O}} [\text{\AA}] )</th>
<th>Site I' occup.</th>
<th>( d_{\text{M-O}} [\text{\AA}] )</th>
<th>Site II occup.</th>
<th>( d_{\text{M-O}} [\text{\AA}] )</th>
<th>Site III occup.</th>
<th>( d_{\text{M-O}} [\text{\AA}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Li}<em>3\text{K}<em>2\text{Al}</em>{12}\text{Si}</em>{18}\text{O}_{48} )</td>
<td>18.6206(3)</td>
<td>–</td>
<td>–</td>
<td>1</td>
<td>2.109(6)</td>
<td>0.168(5)</td>
<td>2.893(6)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( \text{Na}<em>3\text{K}<em>2\text{Al}</em>{12}\text{Si}</em>{18}\text{O}_{48} )</td>
<td>18.5964(4)</td>
<td>0.21(2)</td>
<td>2.743(5)</td>
<td>0.39(1)</td>
<td>2.347(6)</td>
<td>0.851(9)</td>
<td>2.693(6)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>( \text{K}<em>3\text{Li}<em>2\text{Al}</em>{12}\text{Si}</em>{18}\text{O}_{48} )</td>
<td>18.6304(4)</td>
<td>–</td>
<td>–</td>
<td>0.249(7)</td>
<td>2.835(9)</td>
<td>0.983(7)</td>
<td>2.879(6)</td>
<td>0.399(7)</td>
<td>3.318(5)</td>
</tr>
<tr>
<td>( \text{Mg}<em>{2}\text{Al}</em>{12}\text{Si}<em>{18}\text{O}</em>{48} )</td>
<td>18.2499(3)</td>
<td>0.92(1)</td>
<td>2.266(5)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

[a] Site II with an occupancy of 0.168(5) is the residual K\(^+\) in the Li-ZK-5 sample.
oxygen atoms by a distance of approximately 0.45 Å. In Na-ZK-5, Na\(^{+}\) cations are observed in three different sites: Si, Si', and SiI. This is consistent with a previous study.\[^{34}\] As indicated in Table 1, the Na\(^{+}\) site in the puckered 8MRs is more favorable than in the 6MRs, with 85% occupancy at site II. The distances between Na(I)-Na(I) in the same 6MR are too short at 2.136(1) Å to co-occupy these sites at the same time owing to their very high repulsive interactions.

The relatively short distance between Na(I)-Na(I), 4.271(2) Å, is likely to be also repulsive in nature. The total occupancy of Na\(^{+}\) in the 6MR (site I and 2\(\times\)site I') is 0.99(2), indicating that Na\(^{+}\) cations are fully occupied with one Na\(^{+}\) also residing in the double six-membered ring (D6R). The shorter distances between Li-O\(_1\) (O\(_1\) = framework oxygens) compared to Na-O\(_2\) lead to a similar overall displacement out of the 6MR plane in the 6MR (ca. 0.52 Å), even though the Na\(^{+}\) radius is larger than that of Li\(^{+}\).

In contrast to a previous study, only sites I', II, and III were found to contain K\(^{+}\) cations in K-ZK-5.\[^{34}\] K\(^{+}\) was not observed at site I in our model. The highest K\(^{+}\) occupancy was found in the puckered 8MR, which has optimal distance to four framework oxygen atoms. This was also found in the mellite zeolite.\[^{39}\] As the largest of the cations to locate at site I', K\(^{+}\) displaces approximately 1.66 Å out of the 6MR (Figure 4). The distances K-O\(_1\), Na-O\(_2\), and Li-O\(_2\) (Table 1) are close to the predicted sum-of-radii values.\[^{36}\] The distances are larger in sites II, III, and I compared to site I' owing to a higher coordination number of cations in these sites. Furthermore, Na\(^{+}\) interacts more strongly with the framework oxygen atoms in the puckered 8MRs, resulting in shorter Na(I)-O\(_2\) distances than those for K(I)II. This leads to a small contraction of pau-cage and overall a smaller unit cell in Na-ZK-5 compared to Li- and K-ZK-5 zeolites (Table S11).

In contrast with Li\(^{+}\), Mg\(^{2+}\) seems to be more stable in site I despite its small ionic radius, which is also observed in Mg-faujasite zeolites.\[^{37}\] The short distance (2.266(5) Å) of Mg-O\(_2\) compared to the Na(I)-O\(_2\) distance (2.743(6) Å) and higher occupancy of Mg on this site lead to a strong distortion of the D6R in the Mg-ZK-5 sample (Figure 5). Full details of the tetrahedral bond lengths and bond angles for the refinement of cation-exchanged ZK-5 zeolites are provided in Tables S5–S8. The distribution of the tetrahedrally coordinated Si/Al to oxygen (T–O) distances for ZK-5 (Si/Al ≈ 3.65) are reasonable compared to the Si–O and Al–O distances of 1.61 and 1.75 Å, respectively, reported for structures with the feldspar framework.\[^{38}\] for which the weighted average of T–O distances for the feldspar structure with Si/Al = 3.65 is 1.64 Å, and similar to ZK-5 refinements of approximately 1.63–1.64 Å. The average O–T–O angles is 109.5° with small deviations around this value for all samples, in good agreement with tetrahedral coordination. In silicates, the Si–O–Si bond angles are more flexible and lie between 120 and 180° with a mean value near 140°.\[^{39}\] In fact, the Si–O–Si angle is the parameter that shows the greatest variability. In the case of Mg-ZK-5, there is a strong contraction in the Si–O1–Si, Si–O2–Si, and Si–O4–Si angles compared to the M\(^{2+}\) samples. Similar to Na\(^{+}\), Mg\(^{2+}\) occupies site I; however, the higher charge density in Mg\(^{2+}\) leads to a stronger interaction with framework oxygen atoms, resulting in a contraction of Si–O1–Si and Si–O2–Si angles and a shortening of the Si–Si bond lengths, thus suggesting a narrowing of the 6MR (Figure 5). The structural arrangement of CO\(_2\) with the host framework is the dominant contribution to the total adsorption energy as evidenced by the lower Q\(_a\) (Figure 2). The structural arrangement of CO\(_2\) within the ZK-5 framework that allows for as many close contacts as possible should then account for the moderately high CO\(_2\) affinity. Figure 6 shows the CO\(_2\) adsorption site at the center of the flat 8MR window of ZK-5 (site A). This site allows for a total of 24 guest–framework contacts: 8 C–O\(_2\) contacts and 16 contacts of O–O (O = CO\(_2\) oxygen) with distances of 3.2–3.9 Å. The maximum occupancy of site A is 1 based on the zeolite geometry. This results in a total of 12 CO\(_2\) in site A per unit cell or 6 CO\(_2\) per 8MR. As discussed previously, there is a distortion of the other 8MR window (puckered) by the Mg\(^{2+}\) cations, which leads to a decrease in pau-cage size (Table S11); the crystallographic free diameter of the puckered 8MRs is approximately 2.7 Å (d\(_{04-04}\), Figure 5). This is now significantly less than the size of a CO\(_2\) molecule (ca. 2.98 Å).\[^{38}\] These interactions are repulsive, and, as expected, there is no observa-

**Figure 5.** Illustration of the Mg\(^{2+}\) location (green) in site I of zeolite ZK-5, which leads to a contraction of KFI unit cell owing to shorter T–T distances caused by strong Mg\(^{2+}\)-framework oxygen-atom interactions (dashed lines between O2).
electron density in the puckered 8MR as determined by Fourier mapping of the CO$_2$-loaded XRD data. A second adsorption site was located in the paucage based on Fourier mapping of the CO$_2$ scattering density; this adsorption site could be modeled either as site B for which two O atoms of the CO$_2$ are oriented toward the four-membered ring (4MR) of the γ-cage (Figure 7), or as site B* for which two O atoms of the 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Figure 6. CO$_2$ adsorption site A located in the flat 8MR of zeolite ZK-5 (maximum of 6 CO$_2$/α-cage or 12 CO$_2$/uc). Close-contact CO$_2$-framework interactions are shown between O$_2$–O$_2$ (yellow dashed lines) and C–O$_2$ (black dashed lines).

two oxygen atoms of the two closest CO$_2$ molecules in this site is approximately 1.45 Å, too close to be sitting next to each other in the same cage (red dashed lines, Figure 7). Therefore, the maximum occupancy of this site is 0.5, yielding a total of 2 CO$_2$ molecules per γ-cage or 12 CO$_2$ molecules per unit cell in Mg-ZK-5 (Figures S38 and S39).

Further Mg-ZK-5 Fourier-difference analysis also identified a third CO$_2$ adsorption site C located in the large α-cage of the framework (Figures 8 and S40). Site C has a total of 14 close guest–framework contacts. Each CO$_2$ oxygen atom is oriented toward the 6MR in which the Mg$^{2+}$ cations are situated, and each carbon atom has 4 close contacts with the 4MR oxygen atoms. As with site B/B*, the close distance between two neighboring CO$_2$ molecules (red dashed lines, Figure 8) results in a maximum occupancy of 0.34, corresponding to 4 CO$_2$ molecules per α-cage or 8 CO$_2$ molecules per unit cell that can be adsorbed by this site (relative interactions between CO$_2$ sites are displayed in Figure S41). Additionally, it was observed that, upon CO$_2$ adsorption, a portion (ca. 47%) of Mg$^{2+}$ cations relocate from the preferred site I of the hexagonal prism to the 6MR window, similar to the group I cations.

Mg-MOF-74 has been shown to exhibit exceptionally high CO$_2$ adsorption capacity, and the heat of adsorption (47 kJ mol$^{-1}$) is generally higher than for other members of the family (M$^{2+}$ = Mg, Mn, Fe, Co, Ni, Zn).[44] Mg-MOF-74 was determined to have “end-on” CO$_2$ coordination to the unsaturated Mg$^{2+}$ with a short distance of 2.39(6) Å.[8c] The high affinity of Mg$^{2+}$ to coordinate to the CO$_2$ oxygen atom located at ZK-5 site C would overcome the energy penalty for the movement of Mg$^{2+}$ from site I to the less-preferable site I’. The increase of unit cell upon adsorption of CO$_2$ on Mg-ZK-5 is also an indication of a decrease in the population of Mg$^{2+}$ in site I (Table S10). This result is in agreement with a similar increase in unit-cell volume with CO$_2$ adsorbed on Mg-MOF-74, based on periodic DFT-D calculations.[44] Additionally, Mg$^{2+}$ was also found in the 6MR window of faujasite zeolites (site I’, site II) with a high occupancy compared to site I.[37b] The migration of

Figure 7. Adsorption site B in the paucage of Mg-ZK-5 (full occupancy, left); O$_2$–O$_2$ close contacts (green dashed lines) between 3–4 Å and long-range interactions (grey dashed lines) greater than 4 Å (right).

Figure 8. CO$_2$ adsorption site C (C, black; O$_2$, pink) in the α-cage of Mg-ZK-5 (O$_2$ and metal atoms omitted for clarity) with CO$_2$, O$_2$, and cation (Si$^+$)–CO$_2$ close-contact interactions (grey dashed lines, right).

atoms of CO$_2$ are oriented toward the puckered 8MR of the γ-cage (Figure S39). Site B was observed previously when the CO$_2$ molecule fit nicely into the space surrounded by a crankshaft-like arrangement of three 4MRs of the γ-cage in Merlinoite siliceous zeolite.[8a] Refinements of our CO$_2$-dosed XRD data show no statistical preference for one of these two configurations over the other in Mg-ZK-5. Both sites have the same number of close contacts with the zeolite framework oxygen atoms, similar occupancies, and an equivalently good fit of parameters is obtained for each model and each distinct adsorption site as well as mixes of these two adsorption sites (Tables S34 and S35). The site B geometry is illustrated in Figure 7, resulting in a total of 16 O$_2$–O$_2$ and 6 C–O$_2$ close contacts between CO$_2$ and the framework. The distance between
extra-framework cations during the adsorption and desorption process of zeolites has been well documented with various adsorbates.\(^{45,46}\) In this case migration is reversible because the adsorption and desorption isotherms are nearly identical (e.g., at 303 K) and because upon cation migration after CO\(_2\) adsorption at 110 K, the cations revert to their initial position at 298 K as determined by the corresponding refinement of the XRD patterns.

**CO\(_2\) adsorption sites in Li-ZK-5**

Similar to Mg-ZK-5, three different CO\(_2\) adsorption sites were elucidated in Li-ZK-5 from refinement of CO\(_2\)-loaded XPD data. Sites B/B* are the dominant adsorption sites at low CO\(_2\) loadings (Table S10). It is generally observed that energetically favorable CO\(_2\) adsorption sites are found at the center of BMR windows in cation-exchanged zeolites, site A.\(^{21b,31,47}\) Although both site A and site B/B* have the same number of short-range van der Waals (vdW) interactions (total of 16 close contacts between O\(_2\) and O\(_1\), green dashed lines, Figures 7, S38, and S39), the long-range vdW interactions (4–5 Å) contribute somewhat to the adsorption for site B/B*. This is consistent with the preferred adsorption sites for the small alkanes propane and n-butane observed in the small \(\gamma\)-cages.\(^{25}\) Additionally, site B has a small contribution from residual K\(^{+}\) to the adsorption energy owing to an end-on K\(^{+}\)–O–C–O interaction (Figure S42, discussed later). This electrostatic energy also adds to the higher occupancy percentage of site B compared to site A in Li-ZK-5.

The lower occupancy of site C is the result of the fewest number of close contacts of the adsorbate with framework oxygens. If the Li\(^{+}\) were to remain stationary upon CO\(_2\) coordination in the end-on coordination between O\(_2\) and Li\(^{+}\) (ca. 2.3 Å), there would be repulsive close contacts between the CO\(_2\) and the pore walls of the \(\alpha\)-cage. To compensate, the Li\(^{+}\) cations have to shift slightly toward the \(\alpha\)-cages (\(d_{\text{Li}^{+} \cdot \cdot \cdot \text{O}} \approx 2.22\)–2.42 Å compared to \(d_{\text{Li}^{+} \cdot \cdot \cdot \text{O}} \approx 2.11\) Å in dehydrated Li-ZK-5) to form the bridged dual-cation CO\(_2\) complexes between a pair of Li\(^{+}\) (Figure 9). Therefore, the energy loss of Li\(^{+}\) site I’ orienting further from the 6MR is compensated by the strong interaction between CO\(_2\) and two Li\(^{+}\) cations in this site, but the overall interaction is initially weaker than at site A or site B. With increased loading the energetics of each site become similar, although site B saturates first.

**CO\(_2\) adsorption sites in Na-ZK-5**

The distribution of cation sites in Na-ZK-5 compared to the local cation environments observed in Li\(^{+}\) and Mg\(^{2+}\) results in a variation in the electrostatic contributions to the CO\(_2\) adsorption. The addition of a weak long-range electrostatic interaction between both Na\(^{+}\) (I’) and Na\(^{+}\) (II) and the CO\(_2\) located at site A (\(d_{\text{Na}^{+} \cdot \cdot \cdot \text{O}} \approx 4.93\) Å and \(d_{\text{Na}^{+} \cdot \cdot \cdot \text{O}} \approx 5.14\) Å) causes an increase in the dispersive interaction. CO\(_2\) molecules in the pau-cages can only be modelled as site B*, in contrast to Li- and Mg-ZK-5 (Figure 10). The adsorption energy of site B* in Na-ZK-5 is increased by the bridging of CO\(_2\) with two Na\(^{+}\) cations located in the puckered 8MR (\(d_{\text{Na}^{+} \cdot \cdot \cdot \text{O}} \approx 2.49\) Å). The CO\(_2\) molecules at site B* are also further from the zeolite walls than in both Li- and Mg-ZK-5, leading to a reduction of the vdW interaction energy for site B*. CO\(_2\) at site B* orients toward the center of the pau-cage, thus shortening the distance to O\(_1\) site A (ca. 3.00–3.25 Å) compared to that in site B/B* for Li- and Mg-ZK-5 (3.20–3.45 Å).

Fourier-difference mapping of the un-modelled CO\(_2\) electron density is spatially diffuse and could accommodate a bent configuration for CO\(_2\) at site B*. Although large rotational disorder on metal sites could also result in the observed bending angle of CO\(_2\) site B* \(^{38,40}\) a slight bending could be justified through the high interaction of a dual-cation Na\(^{+}\) (II) with CO\(_2\) (ca. 10 kJ mol\(^{-1}\)) higher than a single-cation adsorption site\(^{95}\). The overall energy penalty of approximately 20 meV/CO\(_2\)\(^{48}\) is thermally accessible at room temperature. To test the possibility, we performed refinements of the XPD patterns at a loading of 24 CO\(_2\) molecules per unit cell. Both methodologies resulted in excellent goodness-of-fit parameters for both unrestrained CO\(_2\) (Figure S43) and linearly restrained CO\(_2\) (Figure 10) models for CO\(_2\) at site B* in Na-ZK-5 (Tables S23 and S24).

Na\(^{+}\) occupies only approximately 40% of the site I’, the 6MR window, resulting in CO\(_2\) adsorption at site C that can be considered as single or dual Na\(^{+}\)-cation site (Figure S44). In contrast to Li\(^{+}\), which has to move to bind CO\(_2\), the Na–O\(_1\) distance is sufficiently long that the coordination of Na\(^{+}\) (I’) with framework oxygen atoms remains the same upon interaction with CO\(_2\). Similar to Mg-ZK-5, at CO\(_2\) loadings greater than...
28 CO₂ molecules per unit cell, Na⁺ (I) also partially moves to Na⁺ (II), for which CO₂ would be able to directly interact with the cations (Tables S25 and S26). Polarization of CO₂ by the Na⁺ (and also Li⁺) cations is evidenced by a blue-shift of CO₂ stretching vibrations in the adsorbed phase compared to the gas phase in IR spectra.[224]

CO₂ adsorption sites in K-ZK-5

The K⁺ cation is a moderately soft Lewis acid compared to smaller Li⁺ and Na⁺; therefore, the end-on coordination with the hard basic oxygens of CO₂ is weaker and often results in bridging dual-cation adsorption sites, in which the electrostatic interaction is strengthened by the two cations.[15,31,50] From Rietveld refinements of XPD data, three CO₂ adsorption sites were also elucidated in K-ZK-5 (Figure S45). One K⁺ (site III) is located in the same location of the flat 8MR in which one CO₂ is found (site A); because there is already 0.4 K⁺ there, there is a maximum occupancy of 0.6 CO₂ at this site. At the loading amounts that we studied (less than 18.2 CO₂ molecules per unit cell), the occupancy of CO₂ site A was refined as less than 0.6. There is no evidence of a temporary deviation of K⁺ from the center of 8MR to allow additional CO₂ molecules through a trap-door mechanism.[12] There is also a slight shift of the CO₂ atoms at site A just off the center of the flat 8MRs into the α-cages to avoid repulsive interactions with CO₂ at site B⁺ (Figure S46). The CO₂ site B⁺ has a much longer (ca. 3 Å) K⁺–(II)–O₂ distance (Figure 11). The CO₂ molecule then locates closer to the center of the pau-cages and further from the framework oxygen atoms with only four close contacts (O₂–O₂). There is a maximum of one CO₂ molecule per γ-cage or six molecules per unit cell owing to highly repulsive interaction between CO₂ molecules in the same γ-cage. K⁺ (III) cations have two effects on the adsorption energy of CO₂ site B⁺ if they are adjacent: 1) An increase in electrostatic energy owing to K(III)–O₂ interactions, and 2) a decrease in adsorption energy owing to possible repulsions of K(III)–C (distance ca. 3.2 Å, Figure 11).

Furthermore, CO₂ molecules in the α-cages of K-ZK-5 are very disordered. One possible CO₂ adsorption site is that one CO₂ molecule is bridged to one K⁺ cation in the 6MR and another K⁺ cation in the flat 8MR. This site could also be modeled as CO₂ bonded to two K⁺ cations in a diagonal position of the α-cage owing to the distance between two K⁺ (I) cations along this diagonal position (d_{α-α} ≈ 8 Å) being close to the optimum distance for effective dual-cation adsorption as observed in zeolite K-FER (d_{α-α} = 7.8 Å).[51] Owing to low occupancies of K(III) and K(I)’, these two possible sites are challenging to interpret and model. Therefore, site C was applied to the K-ZK-5 model as an average site for CO₂ in the α-cages as other attempts at refinement of this adsorption did not significantly improve the fit.

Discussion on CO₂ adsorption sites and the relationship with adsorption capacities and heat of adsorption

The structure of solid CO₂ (Figure S37) reported by Simon and Peters indicates that the O atom of one CO₂ molecule is oriented closely to more than 10 oxygen atoms of other CO₂ molecules (contact distances of approximately 3.45 and 3.18 Å) and that each C atom has close contact with 6 oxygen atoms of other CO₂ molecules (d_{C-O} = 3.107 Å).[32] This minimum-energy configuration suggests the importance of vdW interactions, particularly in our case between O–O of both CO₂–CO₂ and CO₂–zeolite. Based on Monte-Carlo simulation, Fischer and Bell suggested that the close contacts between C–O₂ and O₂–Oₖ of 3.3 and 3.44 Å, respectively, lead to a strong dispersive interaction.[84] The optimal interactions of a CO₂ molecule with zeolite frameworks are determined by all neighboring framework atoms because some of the contacts are shorter or longer than the equilibrium distance.

Overall, the KFI-type zeolite containing two different cages has clearly shown multiple adsorption sites over a range of adsorption conditions compared to relatively simple one-cage CHA-, RHO-, and LTA-type zeolites with only two adsorption sites.[21,23,47,52] As mentioned previously, there is an abundance of these close contacts with distances between 3–4 Å for the guest–framework interaction. In Mg-ZK-5, the Mg²⁺ cations situate at the center of the hexagonal prism, which is not accessible to the CO₂ molecules. Moreover, Mg²⁺ is not fully exchanged, so the electric field created by the cation is highly shielded by the six neighboring framework oxygen atoms. This results in a dispersion interaction that is the major contribution to the total adsorption energy in Mg-ZK-5 and explains the much lower heat of adsorption for CO₂ compared to the other Mg⁺-exchanged ZK-5 zeolites. Upon CO₂ adsorption, Mg²⁺ partially moves out of the D6R center to increase the electrostatic interaction by forming a complex with the CO₂ molecules. This increase in the electrostatic interaction compensates for the energy penalty of migrating Mg²⁺ out of a more stable position. Furthermore, the heat of adsorption is almost constant over all CO₂ coverage and close to the values reported for other siliceous zeolites because Mg²⁺ does not affect the over-

Figure 11. CO₂ adsorption site B⁺ in K-ZK-5 showing dual-cation adsorption between CO₂ and K⁺ (III) (purple) in the pau-cage.
adsorption enthalpy as strongly as the cations studied here do.\[54\]

In terms of the remaining monovalent cations, the CO₂–cation interaction and the electric field created by the cations are in the same order as their hardness (Li⁺ > Na⁺ > K⁺). Experimental and DFT-calculation studies in Na- and K-FER also indicate the higher heat of adsorption in Na-FER because of the occurrence of dual-cation sites.\[49\] Furthermore, there are also far fewer close contacts between the framework oxygen atoms and those of CO₂ in the case of K⁺. The ratios of CO₂ occupancies for all three adsorption sites in K-ZK-5 are similar as a function of increased loading amounts, which indicates a similar adsorption energy for each site (Table S10 and Figure S12) and leads to a relatively flat Qₑ. The heat of adsorption increases slightly at high CO₂-loading amounts, probably owing to the contribution of CO₂–CO₂ interactions (Figure S41). Our observation of dual-cation nature in Na-ZK-5 and the great number of close contacts helps explain the highest heat of adsorption for Na-ZK-5, whereas K-ZK-5 shows the lowest value of the monovalent ZK-5 zeolites at low CO₂ coverage. At high CO₂-loading amounts, a steep decrease in the Qₑ is observed for Na-ZK-5. Because the occupancy of Na⁺ (II) is only 0.85, and the occupancy of the CO₂ site B⁺ has a plateau compared to the other two adsorption sites (Figure S11), the accessibility of the higher enthalpy sites is reduced, leading to a decrease in the Qₑ. The population of sites for Na is again somewhat different to the cases of Li⁺ and K⁺ that have a flatter Qₑ at high loading (Figures S10 and S12).

The adsorption-isotherm saturation capacity to 1 bar at 283 K is limited for K-ZK-5 compared to that of the other ZK-5 zeolites. This is a result of the CO₂ adsorption at site B in K-ZK-5 being only half that of the other ZK-5 zeolites and the K⁺ site III competing with CO₂ adsorption at site A. The reduced saturation capacity in Na-ZK-5 arises from neighboring CO₂ molecules occupying site A and site B, with C and O atoms very close (ca. 3–3.2 Å), indicating that CO₂–CO₂ interactions are likely to be more repulsive at high CO₂ loadings. At low temperature (110 K), we refine a CO₂ loading capacity close to that obtained for the Li⁺-exchanged species, indicating that the thermal energy/motion of the CO₂ molecules exceeds some part of the CO₂–CO₂ enthalpy, thus reducing the occupancy. Li⁺ cations are located at the center of the hexagonal prism, as are Mg²⁺ cations in Mg-ZK-5, although neither of them occupies significant pore volume in zeolite ZK-5, thus leaving a higher void volume to accommodate the CO₂ molecules. The CO₂ capacity up to 1 bar in Mg-ZK-5, however, is lowest overall, owing to its low heat of adsorption.

At 110 K, the unit-cell parameters of all cation-exchanged ZK-5 zeolites are larger than those at 295 K (Tables S10 and S11). The negative thermal expansion owing to the changes in Si-O-Si interpolyhedral bond angles, as observed in the contraction mechanism in Mg-ZK-5 described previously, is also well known in chabazite and other zeolite frameworks.\[31,42,54\] There is some evidence that, at 295 K, the γ-cage size of Na-ZK-5 (and Li-ZK-5) decreases slightly upon initial adsorption (Table S11). This is likely a result of the strongest interaction of CO₂ with site B.

Conclusions

In conclusion, we have performed a detailed adsorption and structural analysis of cation sites on Li⁺-, Na⁺-, K⁺-, and Mg²⁺-exchanged ZK-5 zeolites and determined the CO₂ adsorption sites within the ZK-5 framework. Li-ZK-5 displayed the highest CO₂ adsorption capacity at 1 bar pressure and has the highest theoretical saturation capacity based on the CO₂ site distribution obtained from Rietveld refinements. Three different adsorption sites of CO₂ between the flat eight-membered rings, the α-cage, and the γ-cage were elucidated in all four ZK-5 zeolites. XRD provides direct evidence for a migration of the extra-framework Li⁺ (I), Na⁺ (I), and Mg²⁺ (I) cations away from the double six-membered ring (D6R) toward the α-cages upon CO₂ adsorption to form metal–CO₂ complexes. Strong interaction of the high-charge-density cation Mg²⁺ with negative framework oxygen atoms leads to a contraction of the D6R and a decrease of the unit cell is observed in Mg-ZK-5. The addition of CO₂ to Mg-ZK-5 results in an expansion of the unit cell because the Mg²⁺ migrates to accommodate binding to the CO₂. A dual-cation site between two Na⁺ cations at site II and a CO₂ in the γ-cage leads to a high heat of adsorption at low coverage. Owing to the saturation of this site, the isosteric heat of adsorption decreases more sharply in Na-ZK-5 compared to other zeolites. Similar adsorption enthalpies across all three adsorption sites in K-ZK-5, and a corresponding increase in adsorbate–adsorbate interactions, lead to a slight increase in the heat of adsorption with increasing CO₂ coverage. These findings provide a molecular-level understanding of CO₂ interactions in cation-exchanged zeolite ZK-5 frameworks and may aid in further development of new zeolite adsorbents in CO₂-related applications.

Experimental Section

Preparation and characterization of zeolites

ZK-5 was prepared in a manner similar to our previous study\[224\] through a method reported by Schulz and co-workers.\[35\] All starting chemicals were obtained from Sigma–Aldrich\[36\] and used without further purification. Solution A was obtained by dissolving KOH (85 %, 1.64 g) in deionized (DI) water (10 g), to which Al powder (99.9 %, 0.29 g) was slowly added with mild stirring until a clear solution was obtained. Solution B was prepared by dissolving 18-crown-6 (99.0 %, 1.43 g) and Sr(NO₃)₂ (99.0 %, 0.114 g) in DI water (6.3 g), and then Lodox AS40 (8.1 g) was slowly added. Solution B was poured into solution A to obtain a final gel with molar compositions of 10 SiO₂/2 Al/2.3 K₂O/0.1 SrO/1.0 18-crown-6/220 H₂O. The gel was sealed in an autoclave and placed in a convection oven at 423 K for 7 d under static conditions. The solid ZK-5 obtained after filtration was dried overnight at 373 K and then calcined at 833 K for 8 h at a heating rate of 2 K/min. The calcined sample ZK-5 (primarily ZK-5, but with a small amount of strontium) was first exchanged to the ammonium form by mixing ZK-5 (2 g) with NH₄NO₃ (1 L, 1 m) overnight at 353 K. Li-ZK-5, Na-ZK-5, and Mg-ZK-5 were obtained by exchanging NH₄-ZK-5 (0.5 g) and solutions of LiCl, NaCl, and MgCl₂ (500 mL, 2 m), respectively, overnight at 353 K. The exchange was repeated twice. Pure K-ZK-5 was obtained by directly exchanging the original ZK-5 (0.5 g) with KCl (500 mL, 2 m), twice.
The morphological features and chemical compositions of the cation-exchanged ZK-5 zeolites were investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) using a JEOL JSM7400F scanning electron microscope, operating at an acceleration voltage of 3 kV and a current of 10 µA. EDX measurements were taken over at least three different spots and the results averaged. Inductively coupled plasma mass spectroscopy (ICP—MS) measurements were also performed on the Li- and Mg-exchanged ZK-5 zeolites to obtain Si/Al and metal/Al ratios. ZK-5 (Figure S1) consists of cubic crystals with a uniform particle size of 3–5 µm. The results from chemical analysis by ICP and EDX (Table S1) showed that all samples have consistent Si/Al values in a range of 3.5–3.8, and are fully cation-exchanged for Na-ZK-5 and K-ZK-5, and about 75 and 81 % exchanged in the case of Mg\(^{2+}\) and Li\(^{+}\), respectively. There is still residual K\(^{+}\) in the case of Li-ZK-5 owing to the incomplete ammonium-exchange process. Protons are the remaining cations in the Mg\(^{2+}\) and Li\(^{+}\) samples from the ion-exchange or during heating the samples containing residual NH\(_4^+\).

**Volumetric CO\(_2\) adsorption on ZK-5 zeolites**

Micropore surface areas and the pore volumes from Mg-, Li-, Na-, and K-ZK-5 samples were measured from N\(_2\) adsorption at 77 K using a Micromeritics 3Flex device. CO\(_2\) adsorption isotherms were similarly collected for all four ZK-5 samples at 273, 303, and 343 K up to 1 bar pressure. Before the adsorption measurements, each sample was activated (vacuum) at a temperature of 623 K for 6 h.

Data were analyzed according to both dual-site Langmuir (DSL) and dual-site Langmuir–Freundlich (DSLF) models with isosteric heats of adsorption \(Q_0\) determined using the Clausius–Clapeyron equation. More information on the adsorption models can be found in the Supporting Information.

**Diffraction data collection and structure determination**

Synchrotron powder X-ray diffraction (XPD) measurements were performed at the Advanced Photon Source on the 17-BM materials diffractometer \((\lambda = 0.72768 \text{ Å})\) for 10–20 mg samples of activated (dehydrated) Li, Na, K, and Mg-ZK-5 zeolites. The activation procedure for these samples was the same as previously discussed. Activated Li-, Na-, K-, and Mg-ZK-5 samples were transferred into quartz capillaries for the X-ray measurements within an \(N_2\) glovebox. In each instance and after collecting data on the bare sample, the sample was dosed at approximately 295 K with a calculated amount of CO\(_2\) based on the total number of 8MR sites per unit cell, using a custom-built gas-dosing manifold of known accuracy. For some higher CO\(_2\) loadings, data was also collected at 2010 and the CO\(_2\) was allowed to bend and elongate, and to constrain the bond angle to 180° and the CO\(_2\) bond length to \(d_{\text{CO}} = 1.16 \text{ Å}\). If the freeing of the CO\(_2\) molecules did not significantly deviate from the ideal geometry, it was restrained to the ideal. Details of how this affects the overall refinements will be discussed in the appropriate discussion section. Furthermore, atomic displacement parameters (ADPs) and fractional occupations for Ca and O in the same CO\(_2\) adsorption site were constrained to be identical. ADPs were determined for the highest CO\(_2\) dosed in each sample and the ADPs were held constant for the lower CO\(_2\) loading, as refinement of these parameters did not seem to affect the overall quality of the refinement \((R\)-values) or the occupation of the CO\(_2\) molecules. Further details of the crystal structure investigations can be found in the Supporting Information (Tables S12–S35, Figures S13–S36) and in the corresponding cif files, which may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html] on quoting the deposition numbers CSD-432237, -432236, -432235, -432243, -432232, -432223, -432230, and -432229.

Electronic Supporting Information (ESI) is available, containing full experimental details, adsorption isotherms, XPD data and refinements, crystallographic information files (CIFs), and tables of bond distances, angles, and other crystallographic parameters.

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