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The Nature of Chemisorbed CO$_2$ in Zeolite A

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ABSTRACT: Formation of CO$_3^{2-}$ and HCO$_3^-$ species without participation of the framework oxygen atoms upon chemisorption of CO$_2$ in zeolite [Na$_{12}$]-A is revealed. The transfer of O and H atoms is very likely to have proceeded via the involvement of residual H$_2$O or acid groups. A combined study by solid-state $^{13}$C MAS NMR, quantum chemical calculations, and in situ IR spectroscopy showed that the chemisorption mainly occurred by the formation of HCO$_3^-$. We expect that similar chemisorption of CO$_2$ would occur for low-silica zeolites and other basic silicates of interest for the capture of CO$_2$ from gas mixtures.

Adsorption-driven processes for the separation of CO$_2$ from N$_2$ for carbon capture$^{1-3}$ and from CH$_4$ for biogas upgrading$^{4,5}$ are of considerable interest for anthropogenic reasons. Different adsorbents are being extensively studied such as zeolites, activated carbons, porous polymers, and amine-modified silica materials.$^{1,2,6}$ It is generally found that CO$_2$ is typically adsorbed by physisorption,$^7$ but on some sorbents also by chemisorption.$^{8-12}$ For example, on low-silica zeolites with monovalent cations, and to a lesser extent with divalent cations,$^{13}$ CO$_2$ is both physisorbed and chemisorbed.$^{14-16}$ However, to date the mechanisms of chemisorption, and the nature of the species formed, are not well understood. This was the problem we undertook to address in this study, and we were able to identify the species formed from chemisorbed CO$_2$ using a combination of$^{13}$C solid-state nuclear magnetic resonance (NMR), density-functional theory (DFT), and in situ infrared (IR) spectroscopy.

The physisorption of CO$_2$ on zeolites$^{14,19-21}$ is mainly due to the interaction between the relatively large molecular electric quadrupole moment of CO$_2$ and the significant electric field gradients near the zeolite framework. In parallel, low-silica zeolites such as zeolite X,$^{19,22-24}$ Y,$^{15,24,25}$ and A,$^{18,23}$ also chemisorb CO$_2$ resulting in the formation of (H)CO$_3^{1-12}$ species. Even though the positioning of the chemisorbed species at the 8-ring of zeolite A was partially determined by Rzepka et al.,$^{26}$ with in situ neutron diffraction (ND), the precise chemical nature of these (H)CO$_3^{1-12}$ species has remained unknown. It has been speculated that either CO$_2$ reacts with O-atoms of the framework$^{22-25}$ forming framework-linked species,$^{15,16,23,25}$ or that residual H$_2$O or acid groups are involved in forming (H)CO$_3^{1-12}$ species.$^{15,17,25}$

The fraction of chemisorbed CO$_2$ on the system in this study, zeolite [Na$_{12}$]-A, was assessed indirectly by volumetric adsorption measurements$^{18,27}$ of the first two adsorption-desorption cycles, as shown in Figure 1. The reduction in CO$_2$ adsorption capacity in the second cycle relative to the first was ascribed to the fraction of CO$_2$ that had been irreversibly chemisorbed. A long evacuation was used to remove fractionally entrapped CO$_2$, and it was found that approximately 6% of the adsorbed CO$_2$ on zeolite [Na$_{12}$]-A was chemisorbed, corresponding to about 0.5 molecules per α-cage.

![Figure 1](image1.png) Figure 1. The quantity of adsorbed CO$_2$ on zeolite [Na$_{12}$]-A at 293 K for a pristine sample (1st cycle) and after 12h of re-evacuation under high dynamic vacuum (2nd cycle). The data conform to the two-site Langmuir model.

We studied the species formed by chemisorption of CO$_2$ in more detail using in situ IR spectroscopy, as shown in Figure 2.

![Figure 2](image2.png) Figure 2. In situ IR spectra of zeolite [Na$_{12}$]-A under 1 bar of CO$_2$ (a), 0.00003 bar of CO$_2$ (c), and after evacuation under high dynamic vacuum for 4 h (b). In gray: vibrational frequencies and their corresponding C-O stretching modes for CO$_3$/HCO$_3$/CO$_2$ species calculated at the CCSD(T)/cc-pVTZ level of theory.
Characteristic features of the chemisorbed CO$_2$ in zeolite Na$_{12}$-A were observed by the intense C─O stretching bands in the IR spectral range of 1800–1200 cm$^{-1}$. The distinct bands at 1726, 1624 and 1365 cm$^{-1}$ were assigned to HCO$_3^-$ (or other non-symmetrical carbonates), which was supported by the results from \textit{ab initio} calculations shown in Figure 2. The transfer of H-atoms upon formation of HCO$_3^-$ was ascribed to proceed via residual H$_2$O, or from other acidic sites.\textsuperscript{15,17,25} In the literature, the bands at 1726 and 1250 cm$^{-1}$ have been assigned to labile bicarbonate-like species that can be removed upon desorption.\textsuperscript{26} At very low CO$_2$ pressure, and after evacuation (Figure 2b,c), there was a single band of the antisymmetric stretching mode at 1455 cm$^{-1}$ detected, which we attributed to symmetrical and planar CO$_3^{2-}$,\textsuperscript{31} which is corroborated by \textit{ab initio} calculations.

To identify the chemisorbed species, their quantities, and to gain insight into their dynamics, we employed $^{13}$C solid-state magic-angle spinning (MAS) NMR spectroscopy. This technique has been recently and successfully used to investigate the details of chemisorbed CO$_2$ in amine-modified clays\textsuperscript{9} and silicas,\textsuperscript{10} metal organic frameworks,\textsuperscript{11,32} polymers,\textsuperscript{33} and layered hydroxides.\textsuperscript{34} However, $^{13}$C MAS NMR spectroscopy has to date not been used to study the chemisorption of CO$_2$ on zeolites. We note that traditional cross-polarization (CP) approaches have very recently been shown to be problematic in studies of HCO$_3^-$ chemisorbed onto amine-modified mesoporous silica sorbents.\textsuperscript{12} Hence, we employed direct excitation (“Bloch-decay”) NMR protocol with 99% $^{13}$CO$_2$ isotopic labeling to ensure a full visibility of the adsorbed species and quantitative character of the collected data.

The $^{13}$C NMR spectrum at 5 kHz MAS of zeolite Na$_{12}$-A with 1 bar of CO$_2$ is shown in Figure 3(e). Resonances with chemical shifts characteristic of both physisorbed and chemisorbed CO$_2$

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{(a) $\alpha$-cavity of zeolite Na$_{12}$-A; (b-d) the models of CO$_2$ (b), HCO$_3^-$ (c), and CO$_3^{2-}$ (d) species inside $\alpha$-cavity resulting from geometry optimization with the dispersion-corrected OLYP-D3(BJ) DFT approximation and cc-pVTZ basis set. $^{13}$C chemical shifts were calculated with GIAO method at the OLYP/aug-cc-pVTZ-J level of theory (see SI for details). (e) $^{13}$C MAS NMR spectra of CO$_2$ adsorbed in zeolite Na$_{12}$-A collected at 14.1 T and 5 kHz MAS rate. Spinning sidebands marked with asterisks.}
\end{figure}
were revealed. The signals with isotropic positions at 125 ppm and 162 ppm corresponded to physisorbed CO$_2$, respectively. The H-transfer was likely to have occurred with the involvement of H$_2$O or Brønsted acid sites.

No CO$_2^-$ was observed under these conditions. The fraction of chemisorbed species as determined from integrating the $^{13}$C MAS NMR resonances was 0.06 at 1 bar of CO$_2$, which was in an excellent agreement with the fraction estimated from volumetric adsorption data.

The solid-state MAS NMR spectra of Figure 3(e) (bottom and second bottom traces) are from zeolite [Na$_{12}$]-A following saturation with 1 bar CO$_2$, and then subjected to evacuation for 12h under high dynamic vacuum, at temperatures of 298 K and 353K, respectively, and backfilled with 1 bar of N$_2$. In both these cases, the intensity of the signal at 125 ppm was reduced substantially, indicating that very little physisorbed CO$_2$ remains, and the resonances at 162–172 ppm originated exclusively from chemisorbed species. The signals with isotropic shifts at 165 and 162 ppm were hypothesized to correspond to two different types of HCO$_3^-$, whereas at that 172 ppm was attributed to CO$_2^-$.

Similar assignments were reported by Ishihara et al. for the adsorption of CO$_2$ on hydrotalcite. The relative fraction of the CO$_2^-$ to the full amount of chemisorbed CO$_2$ was 0.06 for the system evacuated at 298 K and 0.11 for that evacuated at 353 K. The increased relative fraction of CO$_2^-$ was consistent with a heat- and vacuum-enhanced desorption of CO$_2$ or H$_2$O, which was in line with the in situ IR spectroscopy observations. Concurrently with elevated desorption temperature, there were equilibrium shifts towards higher populations of both carbonates (172 ppm), and bicarbonate species with chemical shift of 165 ppm (at the expense of those with isotropic shift of 162 ppm).

To corroborate the NMR assignments and derive molecular representations of the adsorption of CO$_2$, we calculated the $^{13}$C NMR chemical shifts by using DFT models. The corresponding molecular representations and chemical shifts are presented in Figure 4(b-d). The energy optimized positions of the CO$_2$, HCO$_3^-$, and CO$_2^-$ were in accordance to those refined from ND data by Rzepka et al.

We observed that the calculated chemical shifts were in excellent agreement with those measured experimentally. In particular, we noted that the shifts in Figure 3(c-d) of 163.2 and 174.8 ppm were due to HCO$_3^-$ and CO$_2^-$ ions, and not to physisorbed CO$_2$, which gave a lower shift of 124.8 ppm (Figure 3(b)). At the level of theory employed in the optimization of the DFT models, the potential energy surface did not reveal an energy minimum corresponding to the CO$_2$ binding with framework –O–bridge for any of the several starting configurations used. The calculations indicated that the distance between the C atom of HCO$_3^-$ and the framework O-atom is 3.36 Å (Figure 3(c)), which was in a good agreement with the value of 3.3 Å from the previous ND refinement of the chemisorbed CO$_2$ positions performed for the same system. At this distance, we could infer that there was no participation of the framework O-atom in covalent bonding to the HCO$_3^-$ ion. The same conclusion can be reached for the CO$_2^-$ group (Figure 3(d)), where the C is 3.81 Å from the framework O. Hence, we concluded that both the HCO$_3^-$ and CO$_2^-$ formed as self-standing entities in the zeolite α-cavity without any participation of framework –O–bridge.

To conclude, it is established that the chemisorption of CO$_2$ in low-silica zeolites involves basic sites (conjugate acid-base pairs)$.^{38-41}$ However, in this study we showed for the first time that carbonates did not integrate with the framework of zeolite [Na$_{12}$]-A. We also showed that two different types of HCO$_3^-$ formed and that CO$_2^-$ occurred at very small pressures of CO$_2$. As the formation of CO$_2^-$ is favored only in highly basic environment,$^{12}$ it was consistent that CO$_2^-$ was stabilized at low concentrations of CO$_2$ on the zeolite [Na$_{12}$]-A. We expect that similar equilibria among different coexisting chemisorbed species and their dependencies on the temperature and overall CO$_2$ surface coverage to be observed for other zeolites and basic (alumino)silicates in general.

ASSOCIATED CONTENT

Supporting Information

The detailed methodology of $^{13}$C MAS NMR, quantum chemical calculations, volumetric adsorption measurements, and in situ IR spectroscopy. The parameters of the 2-site Langmuir models for the 1<sup>st</sup> and 2<sup>nd</sup> cycle of adsorption of CO$_2$ in zeolite [Na$_{12}$]-A.

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Notes

The authors declare no competing financial interests.

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Supporting Information for
The Nature of Chemisorbed CO2 in Zeolite A

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S1. Volumetric Adsorption Measurements

The two subsequent isotherms of CO\textsubscript{2} adsorption on zeolite [Na\textsubscript{12}]\textsuperscript{-A} were recorded with a Micromeritics ASAP 2020 surface area and porosity analyzer in the regime of high vacuum-ambient pressure. The sample of zeolite [Na\textsubscript{12}]\textsuperscript{-A} was prepared in ASAP tube, outgassed for 10 h under high dynamic vacuum (0.001\ mbar) at $T = 623$ K, backfilled to 1 bar of dry N\textsubscript{2} at $T = 323$ K and weighted. Free space was evaluated with He gas which is not adsorbed by zeolite A.\textsuperscript{1} The adsorption data were measured with precision of <0.01 \% with the time interval of 15 s. Both isotherms were recorded at the temperature $T = 293$ K controlled by CF31 Cryo Compact Circulator. 0.2 mmol/g incremental dosing mode was applied to register the low pressure regime of CO\textsubscript{2} adsorption. The second CO\textsubscript{2} adsorption isotherm was collected on the same sample after evacuation for 12 h under high dynamic vacuum and $T = 298$ K. Collected data were evaluated according to the two-site Langmuir model:

\[
q = \frac{q_1b_1P}{1+b_1P} + \frac{q_2b_2P}{1+b_2P}
\]

where $q$ is the uptake. \{q\textsubscript{1}; q\textsubscript{2}\} and \{b\textsubscript{1}; b\textsubscript{2}\} are the saturation loadings and Langmuir parameters for sites 1 and 2, respectively, whereas $P$ is the equilibrium pressure. The CO\textsubscript{2} adsorption isotherm parameters and error estimates were obtained with nonlinear regression by sum of squared deviations minimization with the iterative Levenberg-Marquardt algorithm.

| Table S1: Two-site Langmuir isotherm of CO\textsubscript{2} adsorption on zeolite [Na\textsubscript{12}]\textsuperscript{-A}. |
|--------------------------------------------------|
| $q$ \(\text{mmol/g}\) | $b_1$ \(\text{1/kPa}\) | $q_2$ \(\text{mmol/g}\) | $b_2$ \(\text{1/kPa}\) | $R^2$ |
|-----------------|-----------------|-----------------|-----------------|-------|
| \(1^{\text{st}}\) cycle | 3.243 ± 0.008 | 2.787 ± 0.019 | 1.762 ± 0.016 | 0.023 ± 0.001 | 0.999 |
| \(2^{\text{nd}}\) cycle | 2.911 ± 0.011 | 2.692 ± 0.028 | 1.751 ± 0.015 | 0.027 ± 0.001 | 0.999 |

S2. \textit{In situ} IR Spectroscopy

\textit{In situ} IR spectra were collected with Varian 670-IR Fourier-transform infrared (FTIR) spectrometer with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector. The \textit{in situ} gas cell was built of stainless steel high vacuum system and custom-made stainless steel IR transmission cell with KBr windows. The system allowed full control of temperature and pressure.\textsuperscript{2} A 16 mm pellet was made from \~25 mg powder of zeolite [Na\textsubscript{12}]\textsuperscript{-A} under the pressure of 1 ton/cm\textsuperscript{2} applied for 2 minutes. The pellet was outgassed in the IR transmission cell under 10\textsuperscript{-6} mbar at 523 K for 6 h. As a background the IR spectrum of dehydrated zeolite [Na\textsubscript{12}]\textsuperscript{-A} was recorded, hence all presented spectra refer to the adsorbed CO\textsubscript{2}. Pure CO\textsubscript{2} gas (> 99.9\%) was provided by the Linde Gas Company.

S3. Solid-State \textsuperscript{13}C MAS NMR Experiments

Solid-state \textsuperscript{13}C MAS NMR spectra were acquired at a magnetic field strength of 14.1 T (150.9 MHz \textsuperscript{13}C Larmor frequency) with a Bruker Avance III spectrometer. Zeolite samples were evacuated accordingly to those for volumetric adsorption measurements and backfilled with 99\% \textsuperscript{13}C labeled
CO₂ gas supplied by Cambridge Isotope Laboratories Inc. Powders were packed into 7.0 mm zirconia rotors and spun at 5.00 kHz. The data were collected with 6.00 μs radiofrequency (rf) pulses with a spin nutation frequency of 42 kHz. On an average, 1600 signal transients per sample were accumulated with relaxation delay of 60 s. Neat tetramethylsilane (TMS) was used for both, rf pulse calibration and chemical shift referencing.

S4. Quantum Chemical Calculations

For DFT calculations a cluster approach based on molecular orbital calculations was used in order to maximize the accuracy of prediction of the NMR chemical shifts for adsorbed species. Periodic approaches still do not provide enough flexibility with respect to DFT approximation and reliable basis sets for probing core properties. A model of CO₂ chemisorption site in zeolite [Na₁₂]-A was created from the crystallographic coordinates obtained from in situ neutron diffraction data after Rzepka et al.³ Position of the model within zeolite α-cavity is shown in Figure S1. All oxygen atoms on the cluster perimeter were terminated with pseudohydrogens at the distance of 1.000 Å in the direction of missing atoms. Their charges were evaluated to assure that they mimic electrostatics of the lattice beyond the broken bonds. Atomic coordinates of the modelled chemisorbed CO₂ species were optimized without constraints, whereas coordinates of framework atoms were fixed. The Na⁺ cations displacements upon CO₂ adsorption were included in the model, although, as revealed by in situ synchrotron X-ray diffraction experiments were very minor.⁴

![Fig. S1.](image)

All DFT calculations employed the OLYP exchange-correlation functional composed of the OPTX exchange component by Handy and Cohen,⁵ and the LYP correlation part by Lee, Yang, and Parr.⁶ For geometry optimizations DFT-D3 dispersion correction⁷ with BJ-damping⁸ were used and Dunning cc-pVTZ basis set on all atoms.⁹,10 ¹³C absolute shieldings were calculated with the GIAO method.¹¹ The core property aug-cc-pVTZ-J basis set developed by Sauer and coworkers¹² was employed for CO₂/HCO⁻₃/CO₂⁻₃ species in the models, whereas the cc-pVTZ and aug-cc-pVDZ basis sets were used for the Na and zeolite framework atoms, respectively. Further increase of the basis sets sizes or integration grids did not improve results. The isotropic shielding σ_iso⁹ calculated for the ¹³C site j was converted to isotropic chemical shift δ_iso⁹, according to:

\[
\delta_{iso}^j = \sigma_{iso}^{TMS} - \sigma_{iso}^j
\]  

(S2)

where σ_iso^{TMS} is the ¹³C shielding of tetramethylsilane (TMS) obtained at the same level of theory.
The performance of several popular DFT exchange-correlation functionals for the $^{13}$C chemical shift prediction for the CO$_2$ molecule were tested (with CO$_2$ and TMS molecular geometries optimized at the OLYP-D3(BJ)/cc-pVTZ level of theory), and the results are presented in Table S2. Obtained data reveal very good accuracy of the OLYP approximation and justify our choice. In Table S3 equilibrium C–O bond lengths in the CO$_2$ molecule calculated at different levels of theory are presented. These values reveal very good performance of the OLYP-D3(BJ) DFT approximation for molecular geometry predictions in comparison to accurate ab initio methods: second-order Møller-Plesset perturbation theory (MP2), and very expensive coupled-cluster CCSD(T) approach.

For vibrational frequencies, the molecular geometry optimizations of CO$_2$/HCO$_3^−$/CO$_3^{2−}$ species and subsequent numerical calculations of Hessians with cartesian displacement increments of 0.005 Bohr were performed at the CCSD(T)/cc-pVTZ level of theory.

All calculations were done with the ORCA code.$^{13}$

**Table S2: GIAO $^{13}$C isotropic chemical shifts in CO$_2$ molecule.**

| DFT functional/aug-cc-pVTZ-J | $\delta_{\text{TMS}}^{\text{iso}}$ (ppm) | $\delta_{\text{CO}_2}^{\text{iso}}$ (ppm) | $\delta_{\text{CO}_2}^{\text{iso}}$ (ppm) |
|-----------------------------|---------------------------------|---------------------------------|---------------------------------|
| BLYP                        | 178.59                          | 50.57                           | 128.03                          |
| B3LYP                       | 182.35                          | 49.88                           | 132.47                          |
| X3LYP                       | 182.62                          | 49.71                           | 132.91                          |
| OLYP                        | 184.25                          | 59.62                           | 124.63                          |
| O3LYP                       | 184.98                          | 54.77                           | 130.21                          |
| BHANDHLYP                   | 187.08                          | 49.50                           | 137.58                          |
| PBE                         | 182.83                          | 54.63                           | 128.21                          |
| PBE0                        | 187.17                          | 53.74                           | 133.44                          |
| TPSS                        | 189.66                          | 60.32                           | 129.34                          |
| TPSSh                       | 190.59                          | 59.37                           | 131.22                          |
| M06L                        | 190.16                          | 67.68                           | 122.47                          |
| M06                         | 177.57                          | 39.87                           | 137.69                          |
| M062X                       | 179.35                          | 38.65                           | 140.70                          |
| experiment                  |                                 |                                 | 125                             |

**Table S3: Equilibrium C–O bond length in CO$_2$ molecule.**

| Method/cc-pVTZ | $r_{\text{C–O}}$ (Å) |
|----------------|----------------------|
| OLYP-D3(BJ)    | 1.1698               |
| MP2            | 1.1694               |
| CCSD(T)        | 1.1663               |

S4
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