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NMR Reveals Two Bicarbonate Environments in SBA15-Solid-Amine CO_2 Sorbents

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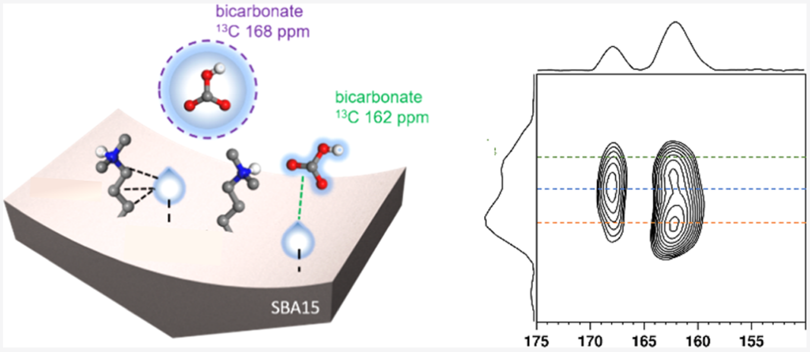

ABSTRACT: We present a spectroscopic study aimed at a better understanding of solid-amine CO_2 sorbent materials that employ amine moieties in mesoporous hosts (here, mesoporous silica SBA15). The materials are exposed to water (or D_2O) and isotopically enriched $^{13}CO_2$ to examine the chemisorption products found with these compositions under conditions relevant to carbon capture from combustion sources. Bicarbonate species have been only recently characterized by solid-state NMR as a product found under humid carbon capture conditions using tertiary amines. Here, we extend these findings to characterize multiple bicarbonate environments (using low-temperature solid-state NMR) associated with not only tertiary but also secondary and primary amine sites using two-dimensional $^{13}C-^{1}H$ heteronuclear correlation (HETCOR) NMR. The use of D_2O provides enhanced resolution in the HETCOR spectra by diluting the protons present and reducing the homonuclear dipolar coupling. One bicarbonate environment is coupled to water present on the walls of the mesoporous silica support, whereas the other bicarbonate is coordinated to water and located in the pore or "mid-channel" while still being coupled to the pendant amine moieties. The identification of bicarbonate in primary and secondary amines, the detection of which was previously obscured by dynamic motion attenuating detection via cross-polarization magic-angle spinning NMR, is presented as well. These findings will help further quantify the presence of both carbamate and bicarbonate in carbon capture materials in the future.

■ INTRODUCTION

Solid-state amine adsorbents are attractive materials for CO_2 capture, compared to amine solutions, and these have more benefits such as lower cost, lower regeneration energy, and less corrosive.[1] Research targeting CO_2 adsorption uptake mechanisms aids in material design, process optimization, as well as identification of adsorption or reaction products. Highly porous supports with amine-bearing moieties either impregnated in the pores or tethered to the pore surfaces are very promising materials for CO_2 separation owing to their low heat capacity and tunable threshold energy to desorb CO_2.[2] Mesoporous silica SBA15 modified with various amine moieties has been shown to effectively capture CO_2, and sorption mechanism studies of aminopropylsilane (APS)-, methylaminopropylsilane (MAPS)-, and dimethylaminopropylsilane (DMAPS)-functionalized materials have identified bicarbonate, carbamate, and carbamic acid as the chemisorbed products upon CO_2 sorption.[3−9]

Solid-state NMR has been successful at studying these various species using ^{13}C and ^{15}N in particular, and NMR methods are well suited to exploring the local environments of the chemisorbed species.[10−14] It has been shown that NMR can detect and quantify the chemisorbed products that contain covalent bonds between amine and CO_2 (e.g., carbamic acid and carbamates); however, bicarbonate has been shown to be more challenging to detect.[15] Humid acid-gas environments

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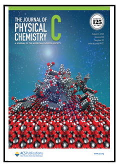

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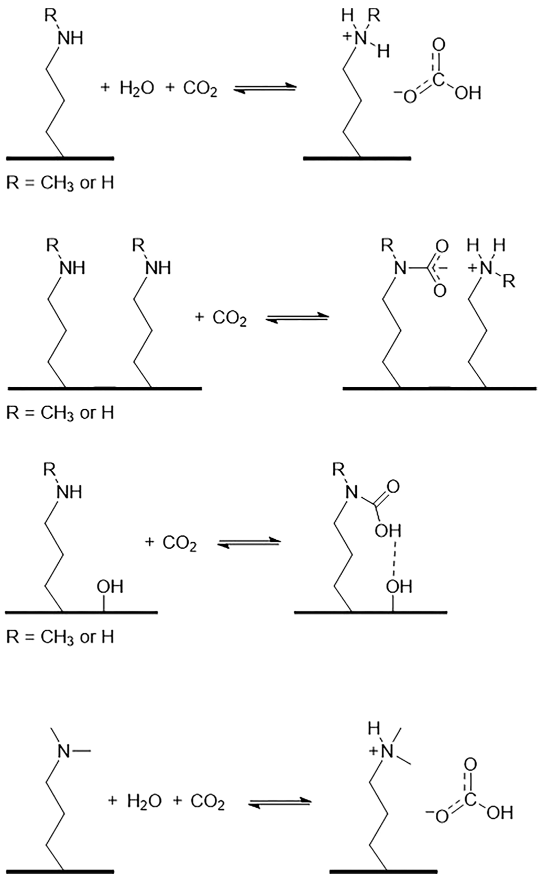
such as those present in flue gas streams can result in different chemisorbed products compared to dry acid-gas environments.[16,17] The presence of water plays an important role in bicarbonate formation, as shown in Scheme 1.[18,19] An important aspect is that the ^{13}C chemical shift of bicarbonate can vary depending on the pH of the system and the local environment.[20] For a tertiary amine in SBA15,[19] where bicarbonate is predicted to be the sole chemisorption product under humid conditions, it has been shown that two bicarbonate species exist.[18] In the primary and secondary amines, the picture is more complex.[21]

Scheme 1. (a) Proposed Reaction of CO_2 with a Primary Amine or a Secondary Amine with and without Water as a Coreactant and (b) Proposed Reaction of CO_2 with a Tertiary Amine in the Presence of Water



Here, we provide a detailed study of the two bicarbonate chemical species formed in amine-modified SBA15 using two-dimensional heteronuclear correlation (HETCOR) NMR spectroscopy. Similar to the earlier work showing multiple bicarbonate species, we have conducted these studies systematically on tertiary, secondary, and primary amines, with a focus on probing the local environment surrounding bicarbonate. This information can ultimately assist in material design since the pendant length, amine density, and degree of steric hindrance at the amine can all be tailored to optimize CO_2 sorption and cyclability.

MATERIALS AND METHODS

Sample Preparation. 3-Aminopropylsilane (APS), *N*-methylaminopropylsilane (MAPS), and *N*,*N*-dimethylpropylsilane (DMAPS) species, all the three pendant species are methoxysilanes, grafted on SBA15, were activated by heating to 105 °C under vacuum at 40 mTorr for 4 h to remove residual CO_2 and water. These silica-supported amine samples are referred to by the acronyms introduced above associated with their silanes. After cooling to room temperature, the sample was then mixed with water and immediately packed into a zirconia rotor. Water was added dropwise to the sample, and equal masses of water and the sample were combined, a 1:1 mass ratio, ~40 mg of water mixed with ~40 mg of the sample. The packed rotor was then placed into a glass tube connected to a gas manifold. One atm $^{13}CO_2$ (Sigma-Aldrich, 99% $^{13}CO_2$) was introduced into the glass tube overnight. The physical properties of APS, MAPS, and DMAPS are as follows: surface areas are 433, 371, and 418 $m^2\ g^{-1}$, pore volumes are 0.56, 0.49, and 0.52 $cm^3\ g^{-1}$, and amine densities are 2.4, 2.5, and 2.1 $mmol_N\ g^{-1}$, respectively.

Solid-State NMR. Low-temperature (~97 K) HETCOR experiments: the HETCOR spectra of $^{13}CO_2$-reacted samples were recorded at 14.1 T using a Bruker 3.2 mm HCN LTMAS probe operating at a ^{13}C frequency of 150.89 MHz and a ^1H frequency of 600.11 MHz. The $^{13}C\{^1H\}$ CPMAS contact time was set to 150 or 500 μs, and a proton decoupling power of 100 kHz was used. The magic-angle-spinning (MAS) rotational frequency was set to 7 kHz, and the recycle delay was optimized and set to 19.5 s. The HETCOR spectrum was obtained with 64 points in the indirect dimension while applying supercycled phase modulated Lee−Goldburg (PMLG)5xx_mm homonuclear decoupling[22,23] optimized as detailed in the literature.[24] The scaling factor (s = 0.59) and proton chemical shift were obtained by applying the sequence under the same conditions to a solid-state glycine sample.

Low-temperature one-dimensional ^{13}C NMR experiments: $^{13}C\{^1H\}$ CPMAS was recorded at 14 T using a Bruker spectrometer equipped with a Bruker 3.2 mm HXY LTMAS probe operating at a ^{13}C frequency of 150.93 MHz and a ^1H frequency of 600.27 MHz. For $^{13}C\{^1H\}$ CPMAS, the contact time was 2 ms and the recycle delay was 10 s at 100 K. The spinning frequency was set at 10 kHz.

RESULTS AND DISCUSSION

Scheme 1a shows the reaction of a primary (APS) or secondary amine- (MAPS) functionalized SBA15 with water and CO_2 to produce both bicarbonate and carbamic acid, along with the methylpropylammonium pendant species. Scheme 1b illustrates the chemical steps involved in the reaction of DMAPS-functionalized SBA15 (or DMAPS for short) with water and CO_2 to produce bicarbonate and dimethylpropylammonium species.

As we and others have shown previously,[18,25] the observed ^{13}C resonance of bicarbonate suggests the reaction of CO_2 with amine groups when water is present that converts CO_2 to bicarbonate, ion-paired with an ammonium pendant molecule (dimethylammoniumpropylsilane). As expected in DMAPS,[18] there is a single ^{13}C bicarbonate resonance (in addition to those of the "backbone" sp^3 carbons tethering the amines to the silica surface). By using isotopically enriched $^{13}CO_2$, an enhanced signal for bicarbonate is found at room temperature. However, unexpectedly, we found that when the temperature is lowered to 100 K, this ^{13}C signal splits into separate resonances. This process is reversible, meaning when the sample is warmed, the two peaks coalesce into one.

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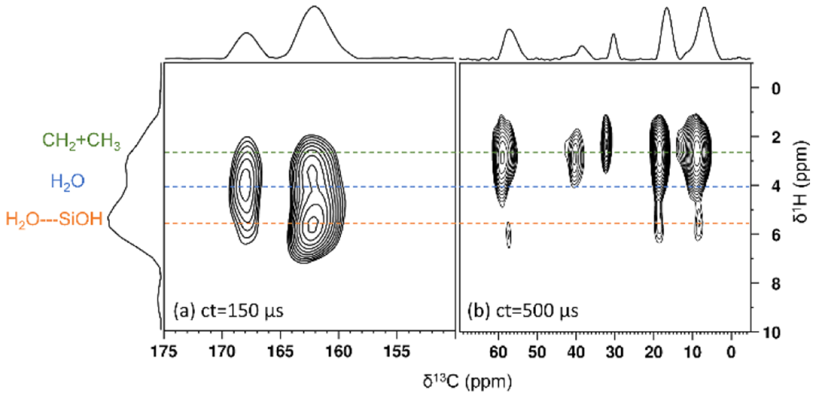


Figure 1. ^{13}C –^{1}H HETCOR solid-state NMR of H_2O-dampened $^{13}CO_2$-reacted DMAPS recorded at 100 K. Two different contact times (ct) were used as follows: (a) 150 (shown on the left for the bicarbonate ^{13}C region) and (b) 500 μs (shown on the right for the aliphatic backbone and pendant methyl carbon regions). Dashed lines are provided as a guide to the eye to better depict ^{13}C–^{1}H correlated features; ^{1}H assignments are given along the vertical axis.

The presence of two resonances demonstrates that the bicarbonate species in the solid-amine sorbent, DMAPS, reside in two separate environments within the material at these low temperatures (SBA15). To determine the nature of these two environments, a ^{13}C–^{1}H HETCOR NMR experiment was performed, as shown in Figure 1, to determine the specific protons to which each of the carbon sites is coupled through dipole–dipole interactions. We have shown previously that the two bicarbonates couple to different protons upon freezing, similar to that shown in Figure 1a.[18] In an attempt to further characterize the two types of bicarbonate, we performed ^{13}C–^{1}H HETCOR with a longer contact time. These HETCOR data were recorded at 100 K to explicitly examine the low-temperature environments. The left side of Figure 1a depicts the bicarbonate resonances that were recorded at a short contact time where the influence of the most proximal protons is the strongest. On the right side of Figure 1b are the aliphatic DMAPS carbon resonances, where a longer contact time was used specifically to search for more distant ^{13}C–^{1}H interactions.

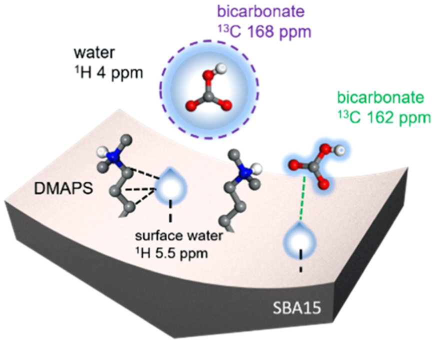
The two bicarbonate resonances appear at 162 and 168 ppm in Figure 1a. Both are coupled to protons from water (^{1}H resonance at approximately 3.8–3.9 ppm), which is unsurprising since water facilitates the reaction. Xu et al. used in situ solid-state NMR to monitor the adsorption of water in porous silica and found multiple water environments including adsorbed water (interacting, hydrogen-bonded, with the surface hydroxide) at δ_{iso}(^{1}H) 5.4 ppm and another water environment at δ_{iso}(^{1}H) 3.8 ppm that does not couple to the surface.[26] We surmise that the ^{13}C resonance at 168 ppm couples to the water that is not hydrogen-bonded to the surface, such as a hydrated bicarbonate in the "middle" of the SBA15 pore structure.

Interestingly, the resonance at 162 ppm is also correlated with a second type of proton that resonates at 5.7 ppm. The cross-peaks to the aliphatic carbons are instructive for its assignment—at a longer contact time (500 μs), the aliphatic carbons are coupled to the 5.7–6.0 ppm ^{1}H resonance. DMAPS is tethered to the surface of the SBA15 silica support, which is known to have a hydrogen-bonded network of surface water molecules present owing to the presence of terminal hydroxyl groups (Si–OH).[27,28] The water on such a surface exhibits ^{1}H NMR resonances that are different from those of "bulk" water, and surface water would be consistent with the cross-peaks to both a near-surface bicarbonate species and DMAPS pendant aliphatic carbons that resonate in this region of the spectrum.

The 162 ppm resonance for bicarbonate also shows a mild skew of the ^{13}C–^{1}H cross-peak to a slightly lower frequency between 2.5 and 3.5 ppm on the ^{1}H scale. Contributions from the coupling of the bicarbonate near the surface to aliphatic sp^3 protons would be consistent with the assignment.

Based on the above observations, we posit that the two different bicarbonate species are composed of a near-surface bicarbonate at 162 ppm and the one that is hydrated and more distant from the surface at 168 ppm, as shown schematically in Scheme 2. Hereafter, we will refer to the two bicarbonate species as "near-surface" (at 162 ppm) and "mid-channel" (at 168 ppm) to distinguish between them.

Scheme 2. Bicarbonate Species Depicted Schematically in Two Environments: One Near-Surface and One "Mid-Channel", More Distant from the Surface[a]



[a]Colored dashed lines are to indicate ^{13}C–^{1}H correlations, matching the color scheme of Figure 1: green to surface-bound water, purple to "bulk" water, and black for the coupling between the aliphatic protons and the near-surface bicarbonate.

To better understand the different bicarbonate environments and get better site resolution in HETCOR experiments, DMAPS was made to react with D_2O and $^{13}CO_2$ to provide a comparison between the results (Figure 2). We recognize that simply using D_2O in the reaction does not wholly exchange all surface-bound H_2O in the SBA15/DMAPS host, and some

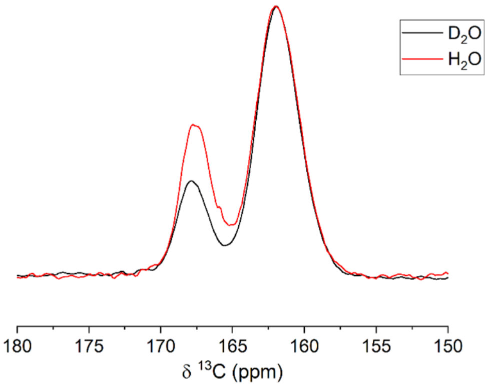


Figure 2. ^{13}C CPMAS spectra (at low temperature, 100 K) of DMAPS reacted with H_2O and $^{13}CO_2$ (red) or D_2O and $^{13}CO_2$ (black). Only the bicarbonate region is shown. The two spectra are normalized to δ_{iso} = 162 ppm resonance for comparison.

water (and hence, ^{1}H) necessarily remains behind. Nevertheless, the D_2O results support the assignments made above.

The ^{13}C mid-channel bicarbonate at 168 ppm is the resonance most affected by the addition of D_2O. The attenuation of its bicarbonate signal (the left resonance in Figure 2) suggests that the environment of this bicarbonate species is becoming less strongly cross-polarized through coupling to a ^{1}H reservoir—consistent with a D_2O-hydrated bicarbonate, with fewer ^{1}Hs in its vicinity. The surface-bound bicarbonate has a larger ^{1}H reservoir to couple to, including the nearby aliphatic protons, as well as any surface-bound water and potential surface Si−OH groups that may not readily exchange with D_2O.

The HETCOR spectrum of the D_2O-dampened sample provides better ^{13}C−^{1}H resolution because deuterium disrupts (or dilutes) the proton "bath" of strongly dipole−dipole coupled water, surface hydroxyls, and bicarbonate−OH protons. Figure 3 shows the ^{13}C−^{1}H HETCOR two-dimensional plot of D_2O-exposed $^{13}CO_2$-reacted DMAPS recorded at 100 K. The enhanced resolution of the cross-peaks for the bicarbonate resonances allows further nuanced assignments to be made.

Both bicarbonates couple to protons at 3.3 ppm, which corresponds to the ^{1}H chemical shift of the aliphatic carbons of the pendant DMAPS species. The coupling of the two bicarbonates to the pendant DMAPS is consistent with our proposed reaction in Scheme 1 and consistent with the literature that bicarbonate is ion-paired to the pendent amine groups,[6,29] noting that both bicarbonates are coupling to these aliphatic carbons of DMAPS, and the 162 ppm resonance is now observed in a distinct (now-resolved) environment at low temperature.

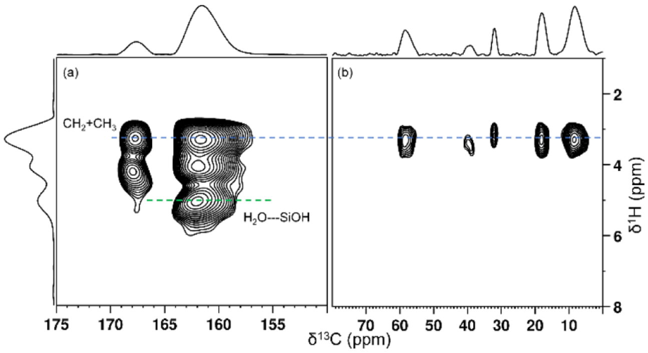


Figure 3. ^{13}C−^{1}H HETCOR solid-state NMR of D_2O-dampened $^{13}CO_2$-reacted DMAPS recorded at 100 K. The contact time was 500 μs: (a) shown on the left for the bicarbonate ^{13}C region and (b) shown on the right for the aliphatic backbone and pendant methyl carbon regions. Dashed lines are provided as a guide to the eye to better depict ^{13}C−^{1}H correlated features; ^{1}H assignments are shown along the vertical axis.

The bicarbonate resonance at 162 ppm is coupled simultaneously to protons in the aliphatic backbone region (∼3.2 ppm), to a proton resonance at ∼4 ppm consistent with "bulk" water, and a third coupling to the surface-bound H_2O at approximately 5 ppm in this spectrum. The aliphatic backbone ^{1}Hs have shifted slightly; however, the absolute chemical shift scale is difficult to establish because of scaling factor difficulties with PMLG decoupling (and the low temperature of the experiment). The lineshape is asymmetric for this resonance, with a shoulder peak extending out to a lower frequency on ^{13}C. As a surface-bound bicarbonate, it is unsurprising that there could be dispersion reflecting anisotropic environments for this type of species.

The second bicarbonate resonance at 168 ppm—that we previously referred to as "mid-channel bicarbonate"—shows a coupling to bulk H_2O (at approximately 4 ppm) but is differentiated from the data of Figure 1 in that a cross-peak to the protons on the aliphatic backbone is resolved here. Since these species are not exchangeable with D_2O exposure, these will be dominant ^{1}H reservoirs to which the ^{13}C of bicarbonate can be cross-polarized for HETCOR. We can rule out the proton from bicarbonate based on the data shown below.

With the knowledge of this splitting of bicarbonate into multiple resonances, it is possible to find this spectral signature in other solid-amine sorbents, such as MAPS/SBA15 (a secondary amine material) and APS/SBA15 (a primary amine material). MAPS and APS both form carbamate[3,5−7,9]—which is seen in the spectra shown in Figure 4—as well as the two bicarbonate environments. These spectra were recorded under identical conditions (same contact time and the number of transients) with a clear indication that little bicarbonate has formed in the APS sample, whereas MAPS has both (note, DMAPS can only form bicarbonate with no reaction to form carbamate). The identification of these environments is critical for accurate assignments, especially when pursuing any low-temperature NMR, such as dynamic nuclear polarization (DNP) or other routes for structural analysis.

It is worth noting that no carbamic acid was observed in APS and MAPS under humid conditions, while this has been observed under dry conditions in our previous studies.[3,12,15] A similar finding was made in the recent work on a related system, amine-grafted SBA15, that carbamic acid formation is not favored under humid conditions.[19] Different ^{13}C isotropic chemical shifts have been reported for primary and tertiary amine samples, noting that there are different experimental conditions such as the sample activation and exposure to humidity between these studies. This variation suggests that the surface chemistry is complex, such that the solid adsorbent reactivity is influenced by factors such as the partial pressure of CO_2 gas, humidity, the nature of amine groups, and the specifics of sample activation.

Finally, an examination of APS, a primary amine, at low temperature can help complete this series. $^{13}CO_2$-reacted APS, dampened with D_2O to facilitate chemisorption reactions, was studied by low-temperature ^{13}C−^{1}H HETCOR NMR, as

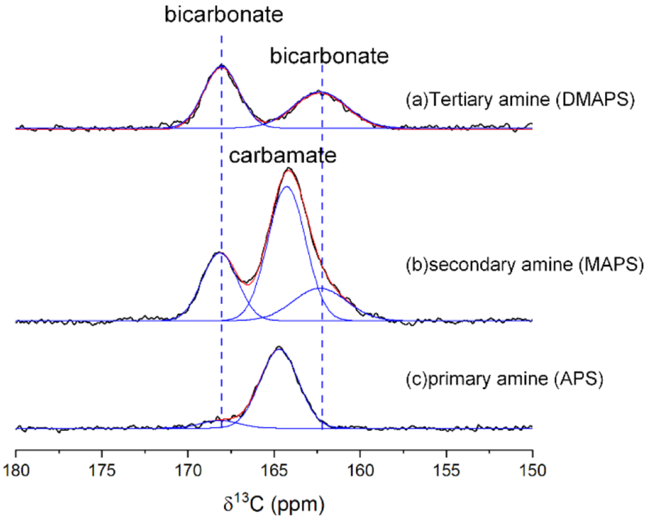


Figure 4. ^{13}C CPMAS of H_2O-dampened $^{13}CO_2$-reacted tertiary (DMAPS) (a), secondary (MAPS) (b), and primary (APS) (c) amine pendant groups in SBA15 recorded at 100 K (contact time = 2 ms, recording 128 transients for each). (All three samples were prepared identically and measured within 3 days of one another in a series.) The region shown is where chemisorption products form—carbamate, carbamic acid, and bicarbonate. Blue dashed lines are at 162 and 168 ppm, where bicarbonate resonances are centered, and in between is where carbamate and carbamic acid fall. Solid blue lines are individual peak fits, while red lines are the sum of all fitted peaks.

shown in Figure 5. The large carbamate resonance dominates the HETCOR plot, with cross-peaks to the aliphatic and H_2O protons, as expected. Even with D_2O being used to mimic humidity in the reacting system, enough protons are present on the SBA15 surface to lead to ^{1}H exchange with surface hydroxyl groups and residual water. Nevertheless, by using D_2O, the amount of ^{1}H−^{1}H homonuclear broadening is attenuated, and better resolution can be seen in the HETCOR data.

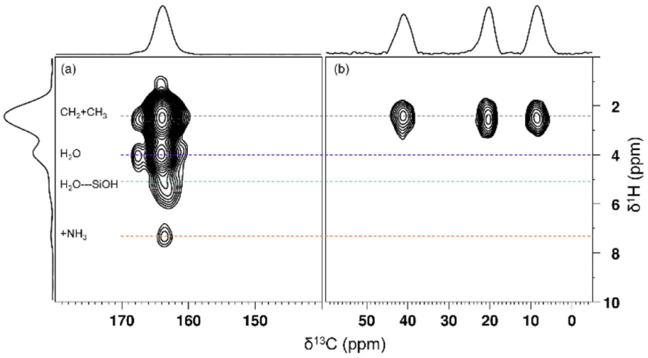


Figure 5. ^{13}C−^{1}H HETCOR of D_2O-exposed $^{13}CO_2$-reacted APS recorded at 100 K: (a) shown on the left for the bicarbonate ^{13}C region and (b) shown on the right for the aliphatic backbone and pendant methyl carbon regions. The contact time was 1000 μs. The dashed lines are guides to the eye: black at the aliphatic backbone methylene groups, purple at “free” water species, green at the surface-bound water, and orange at NH of ammonium.

A new cross-peak is found to carbamate at ~7.4 ppm in the ^{1}H dimension, which we assign to an ammonium species. The resolution also allows a better visualization of the small bicarbonate resonance set off to a high frequency at 168 ppm in the ^{13}C dimension. The cross-peaks are to protons from “free” water (~4 ppm) and a small cross-peak from the aliphatic backbone of the pendant APS. Notably, there is no obvious cross-peak of bicarbonate to the surface H_2O species (expected near 5.5 ppm).

The deconvolution of the peak centered at 164 ppm is shown in the Supporting Information. The resonance can be deconvoluted into three resonances similar to that shown in Figure 4—164 ppm of carbamate and 162 and 168 ppm of bicarbonate. Carbamate has cross-peaks at 2.5 and 7.5 ppm, which are the protons from the carbon backbone and the protons from ammonium, respectively. The correlation of carbamate and ammonium is the evidence of the formation of a carbamate ion pair.

The mid-channel bicarbonate, surface bicarbonate, and carbamate all have cross-peaks at 4 ppm. This finding further confirms that ^{1}H at 4 ppm is the proton of “bulk water”. Since there is substantial water present in the system (likely, ^{1}H-exchanged HOD and D_2O), it is unsurprising that all resonances are correlated with bulk water. We surmise that the proton of bicarbonate is likely obscured by the intense water signal.

The two distinct peaks for the bicarbonates species found using low-temperature NMR provide concrete evidence of the bicarbonate species formation on unhindered primary and secondary amines, which has been debated in studies using Fourier-transform infrared (FTIR) spectroscopy.[6,7] Also, while amine-CO_2 species have been proposed using FTIR spectroscopy in previous studies, their distinct chemical environments with moisture have not been studied in-depth due to the broadness of the IR peaks associated with adsorption species.[4−6] However, the chemical environment that an amine-CO_2 species is in appears to play an important role on its formation on amine sorbents,[16,30,31] elucidating that the hydrogen-bonding environments may give additional insights into determining the favorability of amine-CO_2 species formation on amine sorbents.

■ CONCLUSIONS

We have used two-dimensional ^{13}C−^{1}H HETCOR NMR to explore the bicarbonate chemisorption products evident at low temperature in CO_2-exposed solid-amine sorbents in the presence of excess water. These solid-amine sorbents are DMAPS, MAPS, and APS grafted onto mesoporous silica SBA15. The use of D_2O provides an enhanced resolution of the resonances through the reduction of ^{1}H−^{1}H homonuclear dipolar coupling by diluting the ^{1}H protons on the surfaces and those involved in chemisorption. Through HETCOR, a single one-dimensional ^{13}C spectrum can be shown to be composed of as many as three overlapping components in this study.

We are treating these studies as a model system, rather than an attempt to mimic operando conditions (which would have less water present and designed for sample temperatures between −20 and 100 °C), given the large amount of water present. The low-temperature experiments were carried out to determine the chemical environments of bicarbonate reported previously. Under conditions with sufficient water present, we see the generality of this finding—that two bicarbonate sites exist in primary, secondary, and tertiary solid-amine sorbents. The low temperature permits us to explore the different CO_2 chemisorption environments, evident by solid-state NMR, whose spectra coalesce under dynamic exchange. Two bicarbonate resonances are evident for each of the amines

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(DMAPS, MAPS, and APS) at low temperature because motion is arrested at temperatures below 100 K, while carbamate is evident in the HETCOR spectra, as expected for MAPS and APS. The HETCOR experiments employed two different $^{13}C-^{1}H$ contact times to discriminate between stronger and weaker dipole−dipole interactions, which created an opportunity to observe weaker couplings between the chemisorption products and, for example, the sp^3 carbons of the pendant amines. The two bicarbonate species are assigned as follows: one of the bicarbonates is coupled to water and hydroxides present on the walls of the mesoporous silica support, whereas the other is coordinated primarily to water and located in the pore or "mid-channel". Nevertheless, both show coupling to the grafted amines on the silica surface. This research illustrates the diversity of chemisorption environments in solid-amine sorbents and the persistence of multiple bicarbonate signals across primary, secondary, and tertiary amines when there is an excess of water present.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c04145.

> Detailed spectra of $^{13}C\{^{1}H\}$ CPMAS and $^{13}C\{^{1}H\}$ MAS Bloch decay NMR of H_2O-dampened and $^{13}CO_2$-reacted (APS)-Cabosil and (DMAPS)-Cabosil; low-temperature $^{13}C\{^{1}H\}$ CPMAS NMR of H_2O-dampened and $^{13}CO_2$-reacted APS (DMAPS)-Cabosil and (DMAPS)-SBA15; room-temperature $^{13}C\{^{1}H\}$ CPMAS and $^{13}C\{^{1}H\}$ MAS Bloch decay NMR of H_2O-dampened and $^{13}CO_2$-reacted (MAPS)-SBA15; and deconvolution of the projection of $^{13}C\{^{1}H\}$ HETCOR of D_2O-dampened $^{13}CO_2$-reacted APS recorded at 100 K (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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