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The "Missing" Bicarbonate in CO_2 Chemisorption Reactions on Solid Amine Sorbents

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Supporting Information

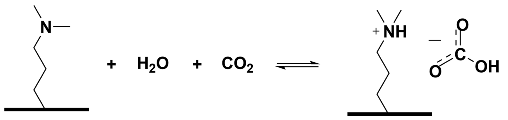
ABSTRACT: We have identified a hydrated bicarbonate formed by chemisorption of $^{13}CO_2$ on both dimethylaminopropylsilane (DMAPS) and aminopropylsilane (APS) pendant molecules grafted on SBA-15 mesoporous silica. The most commonly used sequence in solid-state NMR, ^{13}C CPMAS, failed to detect bicarbonate in these solid amine sorbent samples; here, we have employed a Bloch decay ("pulse-acquire") sequence (with ^{1}H decoupling) to detect such species. The water that is present contributes to the dynamic motion of the bicarbonate product, thwarting CPMAS but enabling direct ^{13}C detection by shortening the spin−lattice relaxation time. Since solid-state NMR plays a major role in characterizing chemisorption reactions, these new insights that allow for the routine detection of previously elusive bicarbonate species (which are also challenging to observe in IR spectroscopy) represent an important advance. We note that employing this straightforward NMR technique can reveal the presence of bicarbonate that has often otherwise been overlooked, as demonstrated in APS, that has been thought to only contain adsorbed CO_2 as carbamate and carbamic acid species. As in other systems (e.g., proteins), dynamic species that sample multiple environments tend to broaden as their motion is frozen out. Here, we show two distinct bicarbonate species upon freezing, and coupling to different protons is shown through preliminary $^{13}C-^{1}H$ HETCOR measurements. This work demonstrates that bicarbonates have likely been formed in the presence of water but have gone unobserved by NMR due to the nature of the experiments most routinely employed, a perspective that will transform the way the sorption community will view CO_2 capture by amines.

Solid amine sorbents capture CO_2 with relatively lower regeneration energy and are less corrosive to equipment compared to the existing aqueous amine solution.[1] However, the mechanism(s) of solid amines reacting with CO_2 are still not fully understood. Three chemisorbed species are proposed based on well-studied reactions with amines: carbamic acid, carbamate, and bicarbonate.[2,3] Carbamic acid and carbamate formed on amines grafted on mesoporous silica SBA-15 have been observed by IR and solid-state NMR (SSNMR) numerous times.[4−11]

The formation of bicarbonate in CO_2 chemisorption reactions on solid amines has been debated in the past.[7,12−15] Solid-state NMR is used extensively to characterize chemisorption products because it can determine structures of these noncrystalline systems and can be employed in a manner that leads to quantification of products, as well as the consumption of reactants, and can detect side products that are formed as well.[16−19] In NMR in particular, the bicarbonate ^{13}C chemical shift appears at a range of values, depending on the environment that contributes to the shielding experienced by the ^{13}C nucleus, and hence is sensitive to surface pH.[20] As a result, bicarbonate moieties may appear at different frequencies in similar samples, and the NMR resonance may even be masked by that of more prominent carbamate or carbamic acid resonances.[21] Carbonate (CO_3^{2-}) is not observed here, because conditions that favor its formation (pH > 11) are not present.

In this work, dimethylaminopropylsilane species (DMAPS) grafted onto SBA-15 was selected as an ideal "model" system for characterization by solid-state NMR (Scheme 1). While tertiary amines such as DMAPS are not of practical importance in carbon capture applications due to their low CO_2 uptake, they have been chosen for study here because they can only adsorb CO_2 by a bicarbonate route in the presence of water. The highly utilized (and studied) primary and secondary amines (such as APS) can adsorb CO_2, forming both carbamate and bicarbonate species. For DMAPS there is no obfuscation of the bicarbonate signal with that of carbamate or carbamic acid, which is critical since all three moieties appear

Scheme 1. Proposed Reaction of CO_2 with DMAPS



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in a similar chemical shift region and are therefore very difficult to discriminate from one another.[22,23]

Figure 1 shows $^{13}C\{^1H\}$ NMR spectra for $^{13}CO_2$-reacted DMAPS that was dampened substantially with water prior to gas exposure (a detailed description of the sample preparation is given in the Supporting Information). Figure 1a is the result of a room temperature Bloch decay magic-angle spinning (MAS) NMR experiment and shows a very narrow (for solid-state NMR) 270 Hz ^{13}C resonance centered at 163 ppm (experiments with and without ^1H decoupling were identical; here ^1H decoupling is included for all experiments for consistency). Figure 1b is a $^{13}C\{^1H\}$ CPMAS spectrum and shows that no signal is observed. (Note: a very small signal can be observed on occasion, with no discernible correlation to experimental conditions). These effects are similar to studies of carbonate in biomineral interfaces.[24,25] Below are two low-temperature 100 K NMR experiments: Figure 1c is $^{13}C\{^1H\}$ Bloch decay MAS NMR, and Figure 1d is a $^{13}C\{^1H\}$ CPMAS experiment. In both, the single room-temperature resonance that was narrowed by dynamic motion now is separated into two species, which are broadened considerably and shifted from that of the hydrated bicarbonate. The similar appearance of the two spectra (Figure 1c and d) shows that both are in hydrogen-rich sites.

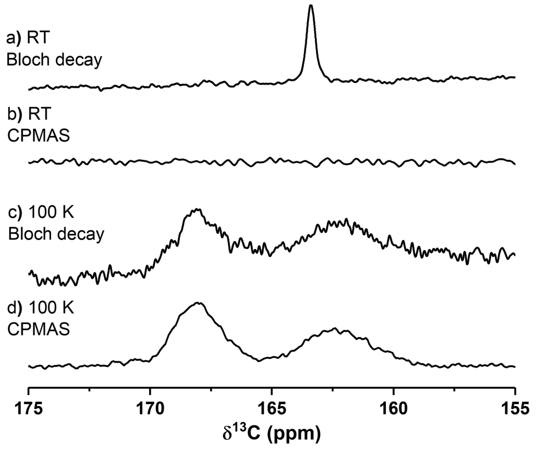

Figure 1. Bicarbonate ^{13}C NMR from CO_2-reacted DMAPS: a) and b) at room temperature (RT) via $^{13}C\{^1H\}$ MAS Bloch decay NMR ("pulse-acquire"), and $^{13}C\{^1H\}$ CPMAS, respectively; c) and d) at 100 K by the same sequences, as indicated in the figure. Rotational frequency for MAS, ν_r, was 10 kHz.

What is significant is that the low temperature experiment shows that $^{13}C\{^1H\}$ CPMAS is now feasible under low temperature conditions where dynamic motion can be arrested. Upon freezing, there is an induced speciation into two magnetically inequivalent sites. We find that the Figure 1 observations can be "cycled" between low and high temperatures, and the speciation is reversible. That is, when the sample is warmed, a single resonance is observed again at room temperature. We surmise that one of the two signals is bicarbonate still surrounded by water, but now "motionally arrested", thereby permitting efficient $^1H-^{13}C$ dipole−dipole coupling. The other resonance is slightly more challenging to assign. The two species are shifted in frequency from one another, indicating these are different chemical environments; however, both species are assigned as bicarbonate, as other forms of chemisorbed CO_2 on tertiary amines are not suggested. Carbonate (CO_3^{2-}) is a possibility in highly basic environments; however, it has not been found in these solid amine systems and cannot be conclusively ruled out. In order to determine the chemical nature of the second species, we look to the example of a related system: $^{15}N\{^1H\}$ CPMAS of pyridine in SBA-15 at 120 to 130 K.[26,27] In this work, two pyridine signals were observed by ^{15}N NMR, assigned to a surface-bound species and a "free" pyridine. At room temperature, one pyridine resonance was observed. Two different characteristic adsorbate sites were identified: a so-called "frozen" conformation arising from interactions with the surface, and one where the adsorbate adopts an "isotropic-like motional state."[28,29]

We have examined a series of spectra over temperatures ranging from 100 K to room temperature. What is evident (selected data shown in the Supporting Information, Figure S2) is the appearance of two-site exchange between these resonances, where the NMR signals arise as a weighted average between two sites, with a "coalescence region" in between. Such exchange phenomena have also been observed in a dipeptide of glycine-(2,2)-d_2-alanine adsorbed on SBA-15 in the presence of minimal amounts of water,[28] at 4 to 7 H_2O molecules/nm^2.

Figure 2 shows a two-dimensional $^{13}C-^1H$ HETCOR NMR data set that indicates two bicarbonate signals are present at low temperatures, but are coupled to different protons, leading to their chemical and magnetic inequivalence. Further experiments are underway to fully characterize these species, but the protons in this region are consistent with H_2O in different environments.[30]

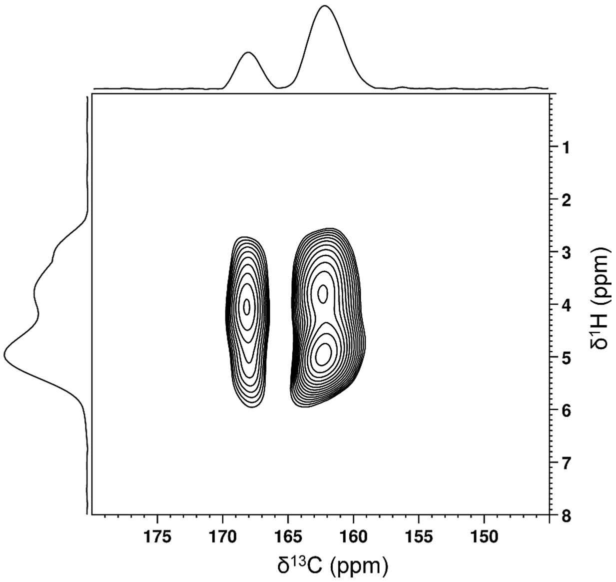

Figure 2. $^{13}C-^1H$ HETCOR of bicarbonate from $^{13}CO_2$-reacted DMAPS at 100 K.

Finally, to demonstrate the generality of the presence of bicarbonate in other pendant amine systems, in Figure 3 we show a pair of NMR spectra for a related $^{13}CO_2$-reacted primary amine pendant molecule, aminopropylsilane (APS), in SBA-15. Adsorbents containing these functional groups have been widely studied by ^{13}C NMR after exposure to CO_2.[5,23] Again, in the presence of water, using $^{13}C\{^1H\}$ MAS Bloch decay, we observe both a bicarbonate signal (at 161 ppm) and a second signal that we have assigned previously[23] at 164 ppm

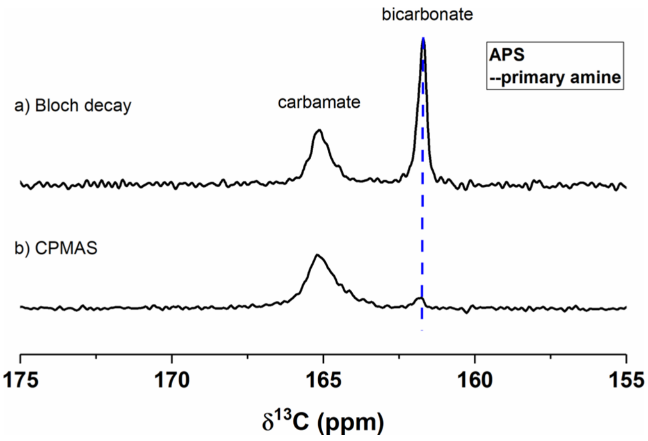

Figure 3. $^{13}CO_2$-reacted "wet" aminopropylsilane (APS) solid-amine sorbent forms both carbamate and bicarbonate, evidenced by ^{13}C NMR at room temperature: (a) via ^{13}C{^{1}H} MAS Bloch decay and (b) via ^{13}C{^{1}H} CPMAS.

to carbamate (Figure 3a). Also, notable in the ^{13}C{^{1}H} CPMAS spectrum shown in Figure 3b is a tiny signal attributable to bicarbonate. Substantial motional averaging of bicarbonate decreases the intensity of this signal when relying on dipole−dipole coupling between ^{1}H and ^{13}C spins in CPMAS. Using conventional data collection procedures at room temperature, the bicarbonate signal is significantly attenuated; therefore, the chemisorption products may potentially be missed or "misassigned" inadvertently by using this standard technique. Because Bloch decay is so infrequently successful owing to the long ^{13}C T_1 relaxation times that are typically found in solids, it is a sequence that is not often employed. Thus, these data show how researchers in the community might have overlooked important chemisorbed products, and therefore it is imperative that both CPMAS and MAS Bloch decay sequences be applied to study these carbon dioxide capture reactions in solid amine sorbents in the future.

In summary, a single narrow resonance at 163 ppm is observed in ^{13}C{^{1}H} Bloch decay NMR of both DMAPS and APS grafted onto mesoporous silica, assigned to bicarbonate. We show in this work, to our surprise, that bicarbonates have likely been formed all along in the presence of water, but they have been missed by solid-state NMR studies due to the nature of the experiments that are routinely employed (namely, ^{13}C CPMAS). We selected DMAPS, a tertiary amine adsorbent, to identify the adsorbed product, bicarbonate, but then extend the methodology to show that the same species also form on a primary amine-containing sample. CPMAS of hydrated bicarbonate formed from DMAPS is only possible at very low temperatures, because it shows dynamic motion caused by surrounding water.[4,22] The motion is arrested at 100 K, where bicarbonate then appears as two chemically distinct species: one that retains a hydrated "shell" and one that we postulate is chemically and magnetically distinct, potentially associated with the surface of the solid-amine sorbent. The two-site exchange model between bicarbonate surrounded by water and surface-bound bicarbonate is consistent with other literature precedent and our data. The dynamic motion of bicarbonate averages out the ^{13}C−^{1}H dipolar interaction, thereby leading to a poor signal in ^{13}C{^{1}H} CPMAS. Therefore, researchers exploring CO_2 adsorption in materials are cautioned to perform both Bloch decay and ^{13}C{^{1}H} CPMAS in order to examine the possible existence of bicarbonate.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b04520.

> Experimental procedures, ^{13}C NMR background from empty coil, and ^{13}C{^{1}H} CPMAS of $^{13}CO_2$ loaded DMAPS at 250 and 223 K (PDF)

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Notes

The authors declare no competing financial interest.

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