

1 Unravelling the structure of chemisorbed CO₂ 2 species in mesoporous aminosilicas: a critical 3 survey

4
5 Rui Afonso, Mariana Sardo, Luís Mafrá*, José R. B. Gomes*

6 CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro,
7 Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

8 *e-mail addresses: lmafra@ua.pt; jrgomes@ua.pt

9 10 **Abstract**

11 Chemisorbent materials, based on porous aminosilicas, are amongst the most
12 promising adsorbents for direct air capture applications, one of the key technologies
13 to mitigate carbon emissions. Herein, a critical survey of all reported chemisorbed CO₂
14 species, which may form in aminosilica surfaces, is performed by revisiting and
15 providing new experimental proofs of assignment of the distinct CO₂ species reported
16 thus far in the literature, highlighting controversial assignments regarding the
17 existence of chemisorbed CO₂ species still under debate. Models of carbamic acid,
18 alkylammonium carbamate with different conformations and hydrogen bonding
19 arrangements were ascertained using density functional theory (DFT) methods,
20 mainly through the comparison of the experimental ¹³C and ¹⁵N NMR chemical shifts
21 with those obtained computationally. CO₂ models with variable number of amines and
22 silanol groups were also evaluated to explain the effect of amine aggregation in CO₂

23 speciation under confinement. In addition, other less commonly studied chemisorbed
24 CO₂ species (e.g., alkylammonium bicarbonate, ditethered carbamic acid and
25 silylpropylcarbamate), largely due to the difficulty in obtaining spectroscopic
26 identification for those, have also been investigated in great detail. The existence of
27 either neutral or charged (alkylammonium siloxides) amine groups, prior to CO₂
28 adsorption, is also addressed. This work extends the molecular-level understanding
29 of chemisorbed CO₂ species in amine-oxide hybrid surfaces showing the benefit of
30 integrating spectroscopy and theoretical approaches.

31

32 **Introduction**

33 Given the negative environmental consequences associated with CO₂ emissions, a
34 great effort has been placed in discovering and developing CO₂ capture solutions, with
35 amine-based solid adsorbents emerging as good sorbent materials¹⁻⁴. This is
36 especially the case for low concentration, low temperature, moisture-containing
37 applications⁵⁻⁷. In the case of direct air capture⁸, companies like Climeworks⁹⁻¹⁰ and
38 Global Thermostat¹¹⁻¹² are already using solid amine-based sorbents. Some cases of
39 post-combustion CO₂ capture have also been proposed for their application¹³⁻¹⁵.
40 Assessing the type of chemisorbed CO₂ structure formed in such porous amine
41 adsorbents is of paramount importance to design and optimise materials for such
42 applications. A recent review article carefully expands on the relation between
43 structure and performance¹⁶.

44 Many researchers have tried to better understand the nature of the CO₂ sorption
45 process on these materials. Although it is well established that chemical reactions
46 (chemisorption) occur upon adsorption of CO₂ in amine covered surfaces, the type of

47 species formed, their stability under different conditions, and the variables influencing
48 their relative proportions are still under great debate. Over the last decades, many
49 studies have presented spectroscopic evidence for the different types of CO₂-amine
50 adducts formed, with a plethora of distinct species being proposed, both for
51 alkylamine-grafted^{1-2, 17-35} and polyimine-impregnated mesoporous silicas^{3-4, 22, 26, 28, 36-}
52 ³⁸. The main species identified were ammonium carbamate^{1-2, 19, 21, 23-25, 27-31, 33-38},
53 carbamic acid^{17-18, 21, 24-25, 28-38} and ammonium bicarbonate^{1-2, 17-18, 22, 29, 33-35, 37-38}, with
54 urea^{22, 24, 27-28} and surface-bonded carbamate (silylpropylcarbamate)^{23-24, 29, 37} forming
55 under special conditions.

56 Traditionally, Fourier-transform infrared (FTIR) spectroscopy has been used as the
57 leading tool in species identification. More recently, nuclear magnetic resonance
58 (NMR) has emerged as a powerful alternative³⁹, able to discriminate not only between
59 different species^{25, 27-28, 30, 34-35, 40-46}, but also different conformations of the same
60 species^{32, 47}. These studies use mainly ¹³C NMR, in order to detect CO₂-amine
61 adducts. Many authors, including our group, were able to observe two ¹³C resonances
62 around 160-161 and 164-165 ppm (Table S20), typically attributed to carbamic acid
63 and carbamate ions, respectively, under different experimental conditions and in
64 different materials^{25, 27, 30, 32, 40-45, 47}. While carbamic acid formation is typically
65 attributed to isolated amines, and ammonium carbamates to amine pairs, it has been
66 shown experimentally and computationally that it is possible to have either paired or
67 isolated carbamic acid^{32, 47}. In addition, an extra peak at 153.3 ppm (Table S20) was
68 observed by our group, which has been attributed to a CO₂ species extremely
69 sensitive to the presence of water, appearing only in absolutely anhydrous conditions.
70 This resonance has been assigned to the presence of isolated amines reacting with
71 CO₂ to form carbamic acid⁴⁷.

72 Pinto et al. ²⁵ were the first to use ¹⁵N NMR to analyse surface CO₂-amine adducts,
73 but the low abundance of the isotope leads to results with an extremely low signal-to-
74 noise ratio. Recent contributions by Jones and co-workers ³⁴⁻³⁵ used a two-step
75 synthesis process to enrich the grafted amines in ¹⁵N, where 3-bromopropylsilane is
76 first grafted onto the silica pore surface, and later ¹⁵NH₃ is made to react with the
77 grafted chains ⁴⁸. By means of ¹⁵N cross polarization magic-angle spinning (CPMAS)
78 NMR, three different amine/ammonium species were assigned to the ¹⁵N resonances
79 associated to amine ($\delta_N \sim 24$ ppm), ammonium siloxide ($\delta_N \sim 32$ ppm) and ditethered
80 amine ($\delta_N \sim 44$ ppm). The latter species appears as an artefact of the unique synthesis
81 procedure employed. Upon adsorption of CO₂, an additional resonance appeared, at
82 $\delta_N \sim 88$ ppm, which has been assigned to carbamic acid and ammonium carbamate
83 species.

84 Herein, a critical survey of all reported chemisorbed CO₂ species formed in primary
85 amine-modified mesoporous silicas is made, by performing new solid-state NMR
86 (ssNMR) experiments, assisted by electronic density functional theory (DFT)
87 modelling calculations. Although some of these CO₂ species have been hypothesised
88 in previous studies, they have never been modelled and this work tries to fill this gap.
89 This work confirms and, in some cases, disproves experimental resonance
90 assignments reported in the literature, while revisiting previous DFT models. In
91 addition, new models are provided which explain the formation of CO₂ species under
92 distinct amine aggregation states. Comparison of experimental and theoretical infrared
93 spectra are also consistent with these assignments.

94 **Experimental section**

95

96 The approach and methods used in the calculations performed in this work were
97 described elsewhere ^{32, 49}. Sample preparation and NMR measurements were
98 performed according to previously reported experimental conditions ^{32, 47, 50}. A detailed
99 description of the used methods and techniques is provided in the Supporting
100 Information.

101

102

103 **Results and Discussion**

104 The most stable structures (*i.e.*, minima on the potential energy surfaces) of the
105 species modelled in the present work are shown in Figures 1 and S2, and the
106 corresponding ¹⁵N and ¹³C calculated chemical shifts (CSs) are presented in Tables 1
107 and S1, respectively. Several starting possibilities for carbonaceous species that may
108 form in silica functionalized with primary amines were considered; for a complete set
109 of structural models please refer to Tables S2-14.

110

111 **Alkylamine and alkylammonium chains**

112 The calculated ¹⁵N CS (Table S1) are in very good agreement with the experimental
113 values (RMSD ~ 2.5±1.4 ppm). Overall, there is a systematic but small positive shift
114 in the calculated values compared to the experimental ones. Such cases occasionally
115 occur when using DFT methods to calculate ¹⁵N NMR CSs ⁵¹⁻⁵³, and were also
116 observed in the case of the aqueous alkylamines considered here to determine a

117 reference root-mean-square error (see computational details and calculated values in
118 Table S25).

119 The clusters used to model amines and ammoniums consider a single amine and a
120 single silanol attached to the silica surface (Figure S2), hence simulating a relatively
121 high amine density but below monolayer coverage. Structural optimisations do not
122 spontaneously lead to the formation of propylammonium siloxide, an *a priori* plausible
123 scenario. Thus, to determine the ^{15}N CS for the ammonium ion, it was necessary to
124 freeze the three N-H lengths at 1.017 Å (typical N-H distance in primary amines and
125 ammonia) during geometry optimisation. This suggests that the adsorbed
126 propylammonium siloxide species (**11**, Figure S2) is far less stable than the co-
127 adsorbed neutral propylamine and silanol groups onto the silica surface (**10**, Figure
128 S2). Indeed, the most stable propylammonium siloxide structure yields a Gibbs free
129 energy of formation 99.6 kJ/mol higher than the most stable neutral amine model
130 (Table S15), which suggests that the former species is very unlikely to form under the
131 conditions assumed in our calculations. This turns out not to be the case in the real
132 system, as discussed further below.

133 Among all species listed in Table S1, the single-tethered amine (**10**, Figure S2) is the
134 one showing the largest deviation between the calculated and the experimental CS
135 values, 27.9 and 24 ppm, respectively. This minor overestimation is typical for ^{15}N CS
136 determination using DFT methods. However, it is still interesting to notice that this ^{15}N
137 resonance reported by Shimon et al. ³⁵, with lower amine concentrations, is slightly
138 more shielded when compared to those of Chen et al. ³⁴, with higher amine
139 concentration. In fact, amine concentrations in Chen et al. are close to monolayer
140 coverage, so interactions with silanols should be relatively rare. It may thus be that the

141 single-silanol, single-amine cluster is more suited to represent the systems of Shimon
142 et al.³⁵ than those of Chen et al.³⁴, from where the 24 ppm value is originally taken.

143 The calculated propylammonium ion ¹⁵N CS (**11**, Figure S2) is remarkably close to the
144 experimental value (33.1 and 32 ppm, respectively), which supports the original
145 assignment³⁴. Although other contributions have previously hypothesised the
146 existence of propylammonium siloxide species^{24, 31, 36-37, 54}, this is the first
147 computational evidence strongly supporting the presence of this species prior to
148 contact with CO₂. The fact that propylammonium siloxide does not occur
149 spontaneously (and is, indeed, much less favoured than the neutral species) in our
150 model, but seems to occur in the real system, may be ascribed to the simplicity of the
151 model employed. From our experience, complex H-bond networks, involving several
152 electronegative atoms and protons, are necessary to stabilise proton transfer in these
153 species. Charged species are often stabilised by water molecules⁵⁵; indeed, the
154 presence of residual water may be fundamental for the formation of propylammonium
155 cations³⁴. Therefore, the formation and stabilization of propylammonium siloxide in
156 the systems studied experimentally can be associated to the presence of either
157 aggregates of silanols and amines at close distance or moisture. The ¹⁵N enrichment
158 method used by Jones and co-workers generates a ditethered secondary amine
159 byproduct. The structure model of this species (**12**, Figure S2) exhibits a calculated
160 CS extremely close to the respective experimental value (45.1 vs. 44 ppm,
161 respectively). As hypothesised³⁴, these species have extremely rigid chains, greatly
162 limiting the number of stable conformations arising from the DFT optimisations.

163 The analysis above confirms that both amines and ammonium siloxide ion pairs are
164 present in aminated silicas, and that under certain synthesis conditions ditethered
165 amines may form.

Table 1. Experimental and calculated ^{13}C and ^{15}N CSs for different CO_2 -amine adducts. Calculated values correspond to the structures shown in Figure 1. Experimental ^{15}C CSs values were taken from the NMR spectra of Figure 2 and from ref. ⁴⁶ (in the case of ammonium bicarbonate). Experimental ^{15}N CSs were taken from ³⁵.

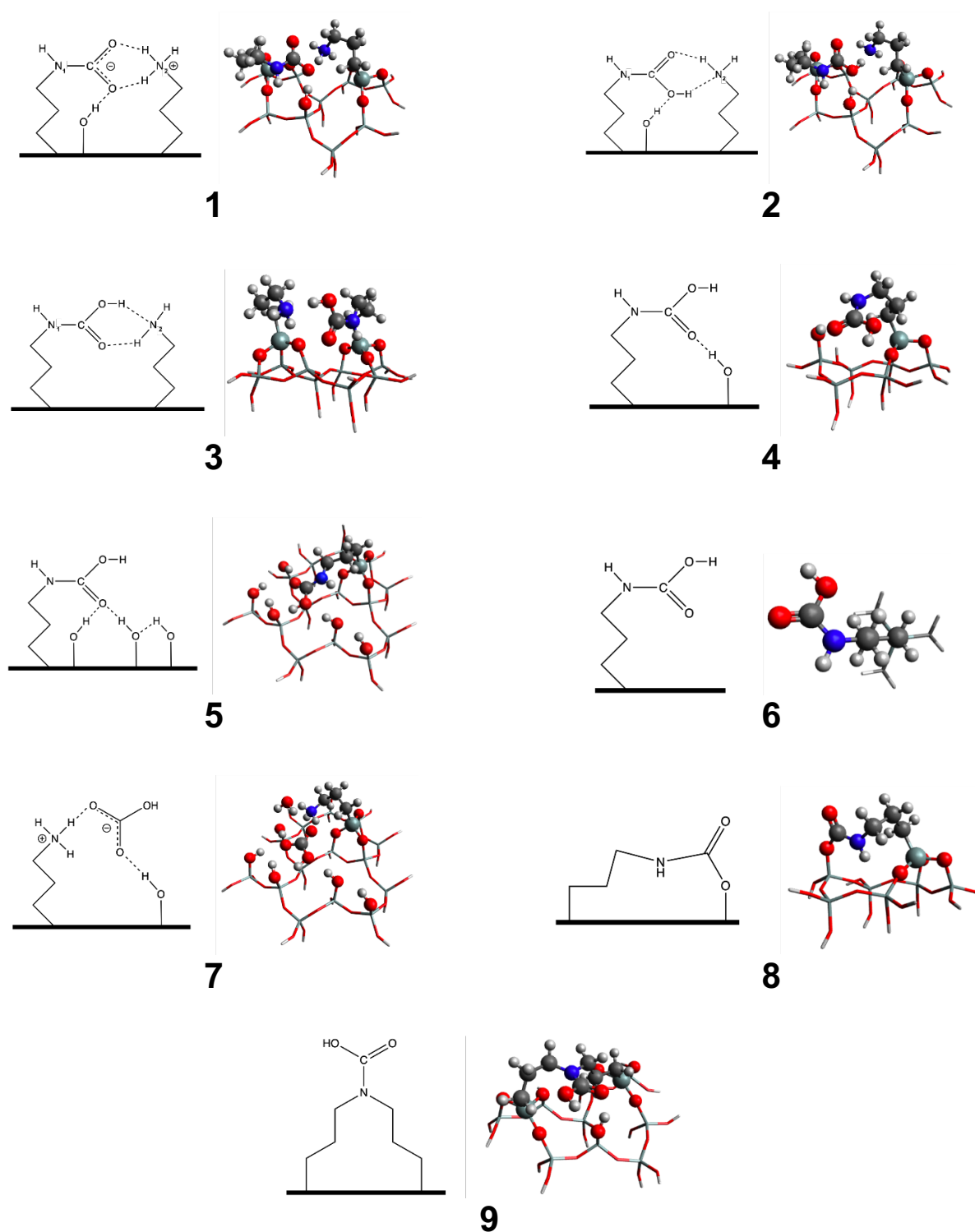
Label	Species	Calculated	Experimental	SI Tables
1	Ammonium Carbamate	$\delta_{\text{C}} = 163.7$ ppm $\delta_{\text{N}1} = 90.4$ ppm $\delta_{\text{N}2} = 34.5$ ppm	$\delta_{\text{C}} = 164.3$ ppm $\delta_{\text{N}1} = 88$ ppm $\delta_{\text{N}2} = 32$ ppm	Table S6 21 Structures
2	Carbamic Acid 2 amines, 1 silanol	$\delta_{\text{C}} = 159.3$ ppm $\delta_{\text{N}1} = 91.2$ ppm $\delta_{\text{N}2} = 31.7$ ppm	$\delta_{\text{C}} = 161.3$ ppm $\delta_{\text{N}1} = 88$ ppm $\delta_{\text{N}2} = 24$ ppm	Table S7 25 Structures
3	Carbamic Acid 2 amines, 0 silanol	$\delta_{\text{C}} = 161.8$ ppm $\delta_{\text{N}1} = 92.6$ ppm $\delta_{\text{N}2} = 31.7$ ppm	$\delta_{\text{C}} = 161.3$ ppm $\delta_{\text{N}1} = 88$ ppm $\delta_{\text{N}2} = 24$ ppm	Table S8 12 Structures
4	Carbamic Acid 1 amine, 1 silanol	$\delta_{\text{C}} = 158.2$ ppm $\delta_{\text{N}} = 83.3$ ppm	$\delta_{\text{C}} = 159.5$ ppm $\delta_{\text{N}} = 88$ ppm	Table S9 5 Structures
5	Carbamic Acid 1 amine, 5 silanols	$\delta_{\text{C}} = 156.1$ ppm $\delta_{\text{N}} = 96.2$ ppm	$\delta_{\text{C}} = 153.7$ ppm $\delta_{\text{N}} = 88$ ppm	Table S10 16 Structures
6	Carbamic Acid 1 amine, 0 silanols	$\delta_{\text{C}} = 153.8$ ppm $\delta_{\text{N}} = 82.5$ ppm	$\delta_{\text{C}} = 152.6$ ppm $\delta_{\text{N}} = 88$ ppm	Table S11 9 Structures
7	Ammonium Bicarbonate	$\delta_{\text{C}} = 162.0$ ppm $\delta_{\text{N}} = 37.5$ ppm	$\delta_{\text{C}} = 162.2$ ppm $\delta_{\text{N}} = 32$ ppm	Table S12 11 Structures
8	Silylpropyl-carbamate	$\delta_{\text{C}} = 147.4$ ppm $\delta_{\text{N}} = 91.9$ ppm	$\delta_{\text{C}} = -$ $\delta_{\text{N}} = 88$ ppm	Table S13 4 Structures
9	Ditethered Carbamic Acid	$\delta_{\text{C}} = 158.5$ ppm $\delta_{\text{N}} = 100.2$ ppm	$\delta_{\text{C}} = -$ $\delta_{\text{N}} = -$	Table S14 9 Structures

167 **Carbamic acid and propylammonium carbamate**

168 A comprehensive analysis of the CO₂ species formed upon reaction of carbon dioxide
169 with alkylamine/alkylammonium molecules has been performed, based on DFT
170 calculations with cluster models that include the propylcarbamic acid/propylcarbamate
171 chain, an unreacted alkylamine/alkylammonium chain and one or more surface silanol
172 groups (up to five silanol groups), as shown in Figure 1.

173 ¹³C solid-state NMR enables the distinction between carbamate ion pairs and
174 carbamic acid, the former with a peak at 160-161 ppm and the latter at 164-165 ppm
175 ^{25, 32, 34} (Table S20). The calculated ¹³C CS of the most stable structures representing
176 these two species have been already reported by us ³². We have recently shown that
177 propylammonium carbamate ion pairs could be identified by the extreme sensitivity of
178 ¹³C chemical shift anisotropy (CSA) to proton transfer ⁴⁷. Moreover a model of
179 carbamate ion pairs, where proton transfer from a COOH group to a neighbour amine
180 was forced, could also reproduce well the experimental ¹³C CSA tensor components
181 ⁴⁷, albeit at the expense of a high energy (i.e., 30 kJ/mol less stable) carbamate ion
182 pair model.

183



185 **Figure 1.** 2D and 3D structural representations of different CO₂-amine adducts. Corresponding
 186 calculated and experimental NMR parameters are presented in Table 1. 3D representations are lowest-
 187 energy optimised structures. Stick and ball-and-stick representations denote frozen and fully optimised

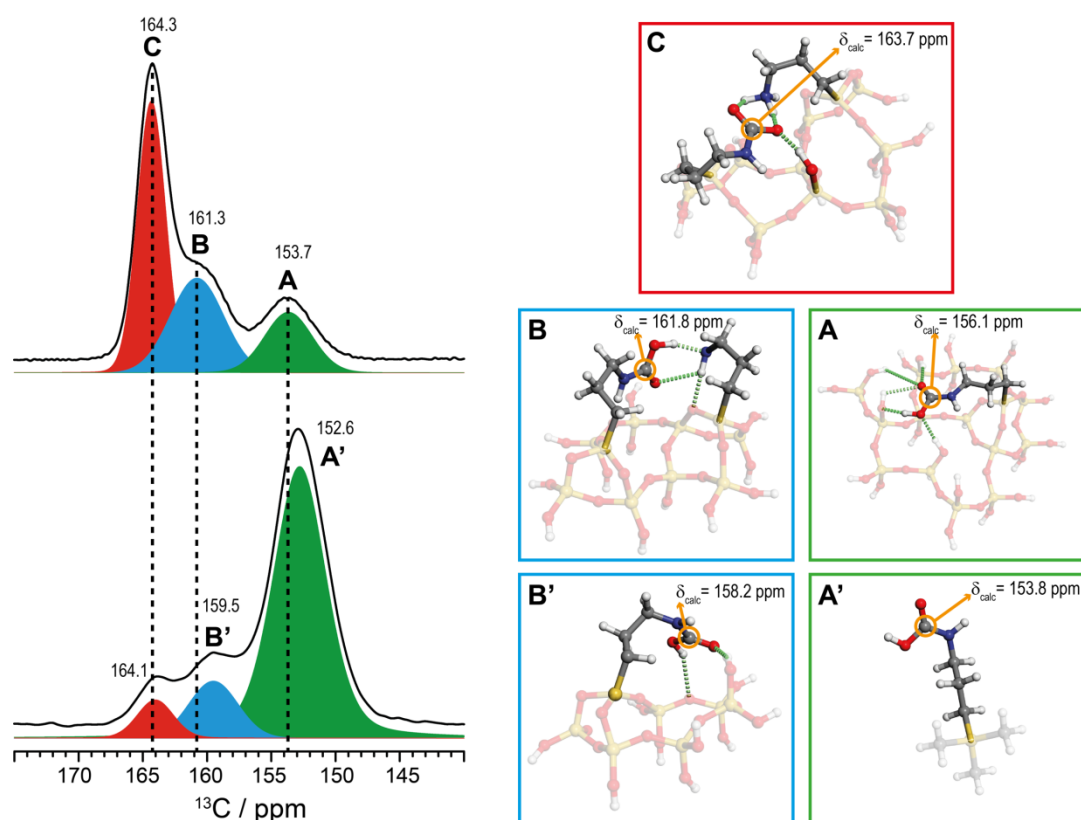
188 atoms, respectively. Colour code is: white, H; dark grey, C; blue, N; red, O; and light grey, Si. Numbering
189 as in Table 1.

190
191 It was possible to find in this work, models of carbamic acid and carbamate structures
192 possessing very similar stabilities (with the latter being less stable than the former by
193 only 3.6 kJ/mol, Table S16). Several different initial configurations containing
194 alkylammonium carbamate ion pairs were built albeit the geometry optimisation runs
195 originated neutral species at the end. Ionic species could only be studied by freezing
196 the three N-H bond lengths of the ammonium species to 1.017 Å. However, it is worth
197 mentioning that one of the initial structures (**1**, Figure 1) led to the formation of the
198 ammonium carbamate ion pair without imposing geometrical restrictions. Indeed, this
199 was the only initial model from the dozens studied in this and in our previous works
200 where the charged species were stable without necessitating to freeze the three N-H
201 bond lengths of the ammonium species. This shows the important role that hydrogen
202 networks may have on the stabilisation of the distinct carbonaceous surface species.
203 In this case, there is a silanol species in the neighbourhood of the carbamate ion that
204 stabilizes the ammonium carbamate ion pair. In fact, the obtained carbamate ion pair
205 model exhibited much lower Gibbs energy than those reported in the previous works.
206 The conformer obtained is thus another strong indication that the commonly observed
207 ^{13}C resonance at $\delta \sim 164.3$ ppm ($\delta_{\text{calc}} = 163.7$ ppm), labelled as **C** in the ^{13}C CPMAS
208 spectra of Figure 2, corresponds to an alkylammonium carbamate ion pair. The
209 nitrogen nucleus of the carbamate moiety of the corresponding structure (**1**) resonates
210 at $\delta_{\text{calc}} (^{15}\text{N}) = 90.4$ ppm ($\delta_{\text{exptl}} \sim 88$ ppm).
211 ^{15}N CPMAS NMR spectra in two recent studies³⁴⁻³⁵ have shown that carbamic acid
212 and propylammonium carbamate contribute to a single resonance at 88 ppm. The

213 calculated ^{15}N CS of the various models considered for these two species, which are
214 listed in Table 1, are in good agreement with this experimental result.

215 $^{15}\text{N}\{^{13}\text{C}\}$ rotational-echo double-resonance (REDOR) data has also been employed
216 show that labelled carbon dioxide binds to the amine group, resonating at 88 ppm
217 (^{15}N), and to derive an internuclear ^{15}N - ^{13}C distance of 1.45 Å ³⁴. A similar distance
218 was obtained by Huang et al. ⁴². However, in our structural models of carbamic acid
219 and ammonium carbamate, N-C distances around 1.36-1.37 Å were obtained, a range
220 that is, nevertheless, in close agreement with the typical distances observed for
221 carbamate ⁵⁶⁻⁵⁹ and carbamic acid ⁶⁰⁻⁶¹ crystallographic structures.

222



223

224 **Figure 2. Left:** ^{13}C CPMAS NMR spectra of $^{13}\text{CO}_2$ -loaded APTES@SBA-15 (mesoporous silica) with
225 high (**top**) and low (**bottom**) amine loadings. **Right:** Clusters used to model the different ^{13}C resonances
226 present in the two spectra. A' and B' are used to represent the A and B resonances in the low amine

227 loading spectrum (**bottom**). Colour code for atoms: grey, C; red, O; blue, N; white, H; yellow, Si. The
228 silica surface model was intentionally faded out to better emphasize the propylamine chains.
229 Resonance C is associated with model **1** from Figure 1, resonance B with **3**, resonance B' with **4**,
230 resonance A with **5** and resonance A' with **6**.

231

232 Many authors, including us, have tried to investigate how amine loading impacts the
233 nature of CO₂ species formed in silica-based materials^{29, 47, 62-63}; however,
234 computational studies modelling CO₂ structures in conditions of high- and low-amine
235 loadings are extremely scarce⁴². Whether CO₂ species are isolated or establishing
236 hydrogen bonds with neighbouring amines, with or without the involvement of
237 hydrogen bonded silanol groups, is still very debatable and very difficult to verify
238 through experimental evidence. To shed light on this matter, it is highly convenient to
239 study materials with the highest and lowest (without compromising detection limits
240 associated to certain spectroscopic techniques) possible amounts of amine coverage
241 in common silica-based materials. To achieve this goal, two amine-functionalized
242 SBA-15 materials have been prepared. One where the amine loading is relatively high,
243 *i.e.*, 2.8 mmol·g⁻¹, and a second where chemical control of amine-amine distances has
244 been performed through the insertion of “bulky” tert-butylcarbamate protecting group
245 into 3-aminopropyltriethoxysilane (APTES) prior to the grafting procedure, which is
246 then readily released upon heating, leaving behind isolated amine groups grafted
247 within the pores. The synthetic route to accomplish this chemical transformation has
248 been taken from ref.⁴⁷ and yielded 0.5 mmol of amines per gram of SBA-15 material.
249 This ensures that amines are at least sufficiently spaced from each other. Figure 2
250 shows how the ¹³C CPMAS NMR spectra are affected by this modification.

251 Figure 2 depicts the full assignment of the ^{13}C resonances in a sample that was
252 meticulously prepared by packing the NMR rotor (sample holder) under rigorous
253 conditions that warrant complete absence of moisture and full control of CO_2 partial
254 pressures⁴⁷. In materials containing high-amine loadings, it was shown that species
255 **A** and **B** are both associated to carbamic acid^{32, 47}. Interestingly, while **C** species
256 appears approximately at the same CS position, regardless of the amine loading
257 employed (Figure 2), resonances **A** and **B** become slightly shifted to a lower CS region
258 (**A'** and **B'**) upon amine dilution. The difference is markedly visible for resonance
259 **B**→**B'**, which shifts almost 2 ppm. Note that the intensities of resonances **C** and **B** are
260 inverted with respect to **A** when the NMR spectra associated to the high- and low-
261 amine loadings are compared. This seems to indicate that paired amines (**B** and **C**)
262 become scarce or vanish upon amine dilution. To check whether the observed ^{13}C
263 resonance shifts, at low amine loadings, are associated to the loss of paired CO_2
264 species (*i.e.*, only isolated carbamic acid species are favoured), new cluster models
265 have been generated to calculate ^{13}C CS in various conformations of non-paired
266 carbamic acid. We denote these new models as **B'** and **A'** in the rightmost side of
267 Figure 2.

268 Isolated carbamic acid (non-paired) was modelled using different silica surface
269 chemical environments; i) gas phase (*i.e.*, not interacting with any silanol), ii)
270 interacting with one Si-OH and iii) interacting with an excess of Si-OH (up to five silanol
271 groups). The lowest-energy models are shown in Figure 1. All the other models
272 containing different combinations of silanol groups can be found in Tables S7-S11,
273 ranked by their total energies.

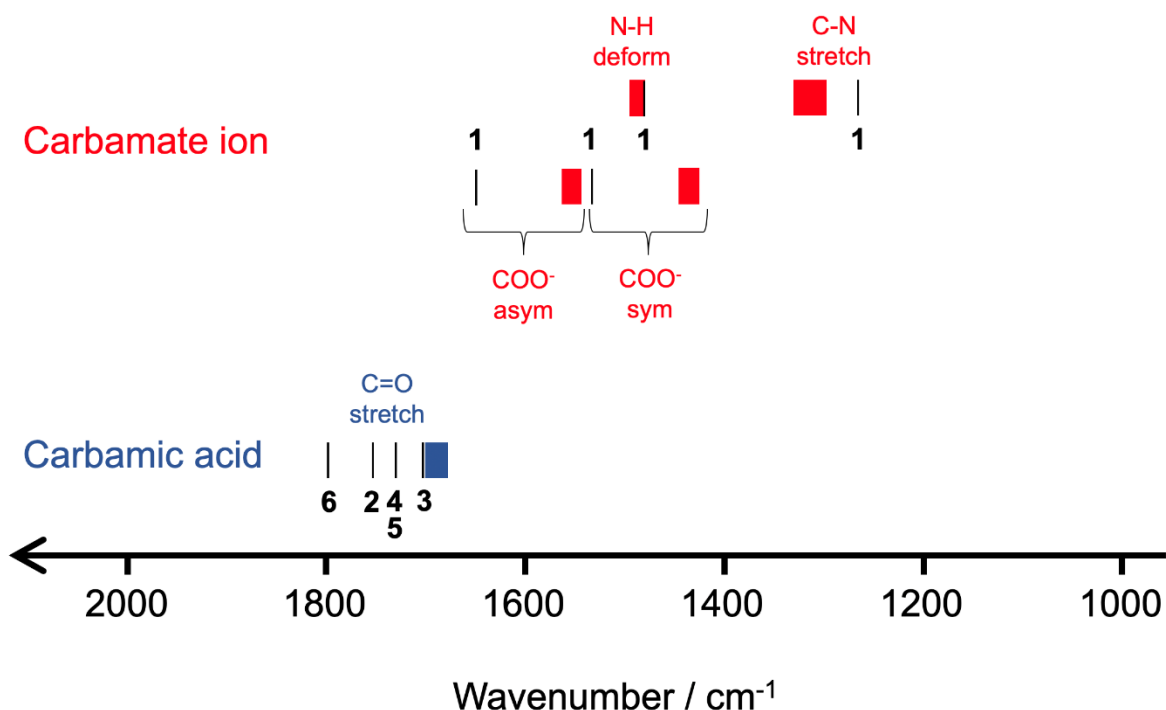
274 A model capable of reproducing the experimental ^{13}C CS of resonances **C** (164.3 ppm)
275 and **B** (161.3 ppm), could not be reached among the generated non-paired carbamic

276 acid models (Table S9-S11), except for much higher-energy clusters from which
277 resonance **B** could be modelled. It is remarkable that the two lowest-energy models
278 obtained for isolated carbamic acid (Table 1 and Figure 1, **4** and **6**) fit very well the
279 experimental CS values of resonances **A'** ($\delta_{\text{exptl}} = 152.6$ ppm vs. $\delta_{\text{calc}} = 153.8$ ppm) and
280 **B'** ($\delta_{\text{exptl}} = 159.5$ ppm vs. $\delta_{\text{calc}} = 158.2$ ppm). It should be mentioned that model **6** refers
281 to a gas phase carbamic acid, which is hypothesised to model a scenario where
282 hydrogen bonding involving silanol groups is not possible. Note that this was the only
283 model that best-fit the experimental resonance **A'** further supporting the fact that this
284 isolated CO₂ species is not interacting with oxygen atoms in its vicinity.

285 Although resonances **A'** and **B'**, appearing in the ¹³C CPMAS NMR spectrum of the
286 sample treated to quench the pairing of propylamines, are very likely associated with
287 isolated CO₂ species, we shall remain sceptical and cannot disregard the possibility
288 to form minor quantities of paired amines that could give rise to CO₂ species
289 resonating at similar frequencies. However, given that resonance **C** does not shift
290 makes sense because: i) this is the CO₂ species associated to ammonium carbamate
291 ion pairs, where amine pairing is mandatory for its existence, and ii) this resonance
292 becomes the species with the smallest intensity, which is fully compatible with the idea
293 of having only a very small quantity of paired amines “surviving” under conditions of
294 extreme amine dilution.

295 Overall, the DFT models of “paired” and “isolated” CO₂ species seem to explain the
296 slightly shielded resonances **A** and **B** (to become **A'** and **B'**), while **C** remains in the
297 same CS upon amine dilution. This leads us to conclude that CO₂ speciation can be
298 far more complex than expected. In fact, several distinct CO₂ species can co-exist
299 depending on the number of silanol groups neighbouring the grafted amines, and on
300 the possibility of eventual amine-amine pairing.

301



302

303 **Figure 3.** Typical ranges (filled boxes) of characteristic wavenumbers of carbamic acid and carbamate
304 ion, collected from experiments in the literature ^{19, 21, 23-24, 29, 31, 33, 54, 63-66}. Corresponding calculated
305 values from this work (labelling as in Figure 1 and wavenumbers in Table S21) are represented by black
306 lines.

307

308 A significant number of studies involving CO_2 speciation in amine-functionalised silicas
309 has been performed using FTIR spectroscopy. The DFT models used to compute the
310 NMR CSs can also be employed in the calculation of vibrational modes to simulate
311 FTIR spectra that can be compared with the experimental ones. We have made a
312 comprehensive screening of infrared spectroscopic data from different literature
313 sources ^{19, 21, 23-24, 29, 31, 33, 54, 63-66} and compiled the data in the diagram shown in Figure
314 3. This figure shows wavenumber ranges for some of the characteristic frequencies
315 collected from literature for carbamic acid and carbamate ion, together with calculated
316 values from the models shown in Figure 1. Overall, there is a good agreement between

317 calculated and experimental values of N-H deformation and C-N stretching in
318 carbamates, with the calculated value of the latter being slightly lower compared to
319 the experimental value. For COO⁻ asymmetric and symmetric stretching in the
320 carbamate ion and C=O stretching vibrations in carbamic acid, there is a significant
321 overestimation of the wavenumbers relative to the wavenumbers up to ~100 cm⁻¹
322 (Table S21). The distinct carbamic acid models generate significantly different
323 estimates for C=O stretching vibration, in a range of 94 cm⁻¹. The carbamic acid (2)
324 model analogous to that of ammonium carbamate (1) generates an overestimation of
325 55 cm⁻¹.

326 Based on the above discussion, it is suggested that both the ion pair ammonium
327 carbamate and the neutral pair amine-carbamic acid are typically present in aminated
328 silicas that have come into contact with CO₂. Partial charge stabilization in ammonium
329 carbamate necessitates a network of hydrogen-bonds involving this species, which is
330 supported by the observation that its ¹³C NMR resonance is remarkably constant at
331 164-165 ppm. The intricate network of hydrogen bonds is also compatible with its
332 resistance to regeneration by vacuum ³⁵. Carbamic acid is suggested to occur on a
333 range of varying chemical environments. While its characteristic C=O infrared
334 frequency is tightly range-bound, the ¹³C resonance can vary significantly with amine
335 or silanol concentration and moisture.

336

337 **Ammonium Bicarbonate**

338 Formation of ammonium bicarbonate on the surface of amine-functionalised silicas,
339 upon reaction with CO₂ and H₂O, has been asserted since the onset of the field ¹⁻².
340 Working with grafted primary amines, Leal et al. ² were the first, in 1995, to provide

341 some sort of evidence for this claim, by identifying an infrared band at 1384 cm^{-1}
342 associated to C-O bending in bicarbonate. In 2003, Huang et al.⁶⁷ made a similar
343 identification with a band at 1382 cm^{-1} . Many other groups claimed to have detected
344 bicarbonate-specific infrared bands^{17-18, 20-22, 29, 33, 37-38, 46, 54, 65, 68-69}, albeit band
345 assignments reported in these studies are inconsistent. This led some authors to doubt
346 whether bicarbonate was even formed in solid amine-functionalised materials^{23-24, 70-}
347 ⁷¹. Our own results regarding the computed infrared spectrum of bicarbonate (Figure
348 S7 and Table S24) provide some support to the previous identifications of ammonium
349 bicarbonate in samples containing primary amines. In particular, the asymmetric and
350 symmetric COO^- stretching vibrations, identified usually at $1670\text{-}1616\text{ cm}^{-1}$ and 1360-
351 1350 cm^{-1} , respectively, seem to correlate well with calculated frequencies of 1696
352 cm^{-1} and 1385 cm^{-1} .

353 Recent studies show that the use of tertiary amines provides powerful evidence for
354 the formation of bicarbonate in amine-functionalised silicas. For instance, Lee et al.⁴⁶
355 reported a ^{13}C CS of 162.2 ppm for the carbonyl resonance in bicarbonate; as the
356 usual chemisorbed CO_2 species (carbamic acid and carbamate) are only formed in
357 primary/secondary amines and not in bulkier amines. The same authors have also
358 employed $^{13}\text{C}\{^{15}\text{N}\}$ REDOR NMR experiments³⁴, in materials grafted with primary
359 amines, suggesting that 10 % of the observed ^{13}C resonance intensity at 165 ppm
360 could also be associated to ammonium bicarbonate. Still, it is complicated to verify the
361 presence or absence of ammonium bicarbonate in samples of mesoporous silicas not
362 fully degassed (i.e., containing water) modified with primary/secondary amines due to
363 strong resonance overlap with other CO_2 species in this ^{13}C CS region.

364 Our DFT results lend some support to the experimental ^{15}N CS reported elsewhere ³⁴.
365 The ^{15}N CS of the most stable structure model of ammonium bicarbonate (**7**, Table 1)
366 is somewhat larger than that of ammonium siloxide (**11**, Table S1), but not enough to
367 decisively discern it by ^{15}N NMR. Similarly, the calculated ^{13}C CS is relatively close to
368 the experimental value ⁴⁶, *i.e.*, 162.0 and 162.2 ppm, respectively.

369 Our energetic analysis of the bicarbonate stability (Table S18) shows that this species
370 is 12 kJ/mol less stable than carbamic acid, when using single-amine/single-silanol
371 clusters. This suggests that formation of carbamic acid under wet conditions is still
372 favoured. However, this result needs to be taken carefully, as discussed for the
373 amine/ammonium system (see section “Alkylamine and alkylammonium chains”). In
374 fact, it is perfectly possible that bicarbonate forms in some samples and not in others,
375 depending on the kind and concentrations of amines and the type of host material ²⁹,
376 ⁶²⁻⁶³. This could explain why some authors reported a significant increase in the CO_2
377 adsorption capacity of amine-functionalised materials upon introduction of water into
378 the system ^{2-3, 67-69, 72-74}, while others did not ^{19, 24, 70, 75-77}.

379

380 **Silylpropylcarbamate**

381 Formation of silylpropylcarbamate, also known as surface-bonded carbamate, has
382 been proposed in previous publications ^{23-24, 29, 37, 63}, based on interpretations of
383 infrared spectra. Identification of this species was made based on infrared bands at
384 1510 cm^{-1} and 1714 cm^{-1} . These bands could easily be used to propose the formation
385 of carbamic acid, as the authors themselves recognise. In addition, they argue
386 carbamic acid is thermodynamically unstable, and therefore cannot be present,
387 leaving silylpropylcarbamate as the only other alternative albeit carbamic acid has

388 been securely identified in CO₂-exposed amine-functionalised silica, using both
389 infrared^{17-18, 21, 24, 29, 31, 33, 36-37, 54, 64-66} and NMR spectroscopy^{25, 32, 34}. Bacsik et al.²⁴
390 have made a more compelling case for the formation of silylpropylcarbamate. They
391 admitted that samples with low amine concentration might lead to the formation of
392 carbamic acid, but also added that, with time, the latter species condenses with
393 surface silanols to form silylpropylcarbamate. The authors grounded this conclusion
394 on a shift of the vibration associated with the carbonyl peak from 1704 cm⁻¹ to 1715
395 cm⁻¹, from 2 to 60 min after the introduction of CO₂ into the system. Furthermore, the
396 authors observed that the species at 1715 cm⁻¹ was more common in samples with
397 low amine loading and persisted upon CO₂ evacuation and high temperatures. From
398 the same group, Aziz et al.⁶³ used an infrared band at 1700-1695 cm⁻¹ to identify the
399 presence of carbamic acid and silylpropylcarbamate, being unable to distinguish
400 between the two. Didas et al.²⁹ have also postulated the presence of
401 silylpropylcarbamate, although all the infrared bands used for its identification could
402 also easily be attributed to carbamic acid. Yu and Chuang³⁷ mentioned the possibility
403 of formation of silylpropylcarbamate, without providing any evidence. We have
404 simulated the infrared spectrum considering a silylpropylcarbamate model (**8**, Figure
405 1); the calculated frequencies at 1799 and 1479 cm⁻¹ (Figure S6 and Table S23),
406 correspond to C=O stretching and N-H bending modes, respectively. These theoretical
407 vibrational bands do not correlate well with experimental values obtained by the
408 different authors. Our calculations show that the calculated C=O stretching vibration
409 for silylpropylcarbamate is overestimated up to ~ 100 cm⁻¹ (1700 vs 1799 cm⁻¹),
410 considering that the experimental band at ca. 1700 is correctly assigned to this
411 species. This discrepancy further emphasizes how difficult it is to reach definite

412 assignment of CO₂ species on such a complex matrix based solely on FTIR
413 measurements.

414 Very similar calculated ¹⁵N CS ranging from 91.9 to 98.5 ppm (Table S13), were
415 obtained for models of silylpropylcarbamate; the lower ¹⁵N CS limit is rather close to
416 the experimental value (88 ppm) reported by Shimon et al.³⁵. The same comparison
417 cannot be made through ¹³C CS analysis as there is no ¹³C resonance that can be
418 assigned to this species. In fact, according to our lowest energy model (**8**, Figure 1),
419 the calculated ¹³C CS of the silylpropylcarbamate carbonyl yields 147.4 ppm (Table
420 1), which is well outside the typical range of ¹³C CS associated to the observed CO₂
421 species (Figure 2 and Table S20). In addition, the energetic analysis of
422 silylpropylcarbamate (Table S17) shows it to be 30 kJ/mol less stable than carbamic
423 acid, and 15 kJ/mol less stable than adsorbed CO₂, which are significant differences,
424 suggesting that the formation of silylpropylcarbamate in amine-functionalised silicas is
425 thermodynamically unfavourable. Therefore, our results do not support the presence
426 of this species as it was hypothesised by other authors.

427

428 **Ditethered carbamic acid**

429 Previous works³⁴⁻³⁵ assigned the ¹⁵N resonance at 44 ppm to unreactive ditethered
430 amine (secondary amine) species showing that this species remains unchanged upon
431 adsorption/desorption of CO₂. It was suggested in those works that this could be due
432 to the rigidity of the ditethered chain, since secondary amines typically readily react
433 with CO₂. Our results show that ditethered carbamic acid lowest-energy model (**9**,
434 Figure 1) give rise to a ¹⁵N CS at 100.2 ppm, which is ca. 10 ppm higher than those
435 obtained for single-tethered carbamic acid ($\delta_N=91.2$ ppm) and alkylammonium

436 carbamate ($\delta_N = 90.4$ ppm) models (Table 1). This is fully consistent with previous
437 interpretations where the experimental ^{15}N CS of CO_2 -adducts resonates at $\delta_N \sim 88$
438 ppm³⁴⁻³⁵, which is quite far from the calculated value (100.2 ppm). The energy penalty
439 obtained upon the formation of ditethered carbamic acid (**9**), compared to a free amine
440 with nearby physisorbed CO_2 (**12**, Figure S2), is 70 kJ/mol (Table S19). Thus, the
441 formation of ditethered carbamic acid upon adsorption of CO_2 into a silica adsorbent
442 with doubly-grafted amines is excluded.

443 Since hydrogen bonds are fundamental to stabilise the structure of single-tethered
444 carbamic acid, ditethered amine motion is probably hindered to such an extent (when
445 compared to single-tethered amines) that interactions with the surface become
446 difficult, and can only occur with significant straining of the alkyl chains. The hydrogen
447 bond stabilising effect thus seems to be missing in ditethered carbamic acid,
448 explaining the lower stability of this species. A previous study also suggested that
449 interactions with the surface are central to the stabilisation of amine- CO_2 adducts²³.

450 In summary, in this work, an exhaustive survey of the most relevant atomic level
451 studies regarding the chemisorbed CO_2 structure is provided. We revisit the
452 experimental proofs of assignment of the distinct chemisorbed CO_2 species found thus
453 far in the literature by debating results obtained from different authors, highlighting,
454 whenever possible, controversial assignments regarding the existence of certain
455 chemisorbed CO_2 species. A number of structural aspects regarding the formation of
456 certain CO_2 species in mesoporous aminosilicas functionalized with distinct amine
457 loadings have also been revisited by means of DFT calculations of NMR and FTIR
458 parameters based on chemisorbed CO_2 structure models. In particular, the M06-2X
459 functional was used to calculate ^{15}N and ^{13}C NMR CSs, FTIR spectra and Gibbs
460 energies of formation for several CO_2 species that may be present in pristine and CO_2 -

461 loaded aminosilicas. Several structural models were analysed for the first time while
462 others were revisited in order to compare experimental and calculated $^{13}\text{C}/^{15}\text{N}$ CSs
463 and vibrational modes. Calculated Gibbs energies of formation were typically good
464 indicators of the propensity of such species to form, i.e, carbamic acid and carbamate
465 moieties are slightly more stable than bicarbonate, and significantly more stable than
466 silylpropylcarbamate or ditethered carbamic acid, in decreasing ordering of stability.
467 ^{15}N CSs confirmed the presence of three possible species of amine/ammonium in the
468 samples prior to the introduction of CO_2 into the system, *i.e.*, amine, ammonium
469 siloxide and ditethered amine. Calculated ^{13}C CSs, coupled with an experimental
470 assessment, confirmed the formation of several kinds of carbamic acid/carbamate
471 moieties, in CO_2 -loaded materials containing distinct amine loadings. Simulated
472 infrared spectra of carbamic acid and alkylammonium carbamate compared well with
473 typical experimental values, confirming these to be the predominant CO_2 species.

474

475

476 **Acknowledgements**

477 This work was developed in the scope of the projects CICECO-Aveiro Institute of
478 Materials POCI-01-0145-FEDER-007679 (Ref. FCT UID/CTM/50011/2019),
479 PRESSNMR_MAT - P2020-PTDC/QEQ-QAN/6373/2014, GAS2MAT-DNPSENS -
480 POCI-01-0145-FEDER-028747 and Smart Green Homes POCI-01-0247-FEDER-
481 007678, a co-promotion between Bosch Termotecnologia S.A. and the University of
482 Aveiro. These projects are financed by Portugal 2020 under the Competitiveness and
483 Internationalization Operational Program and by the European Regional Development

484 Fund (FEDER). The authors are also thankful to Fundação para a Ciência e a
485 Tecnologia (FCT) for the Investigator FCT program (LM and JRBG).

486

487

488 **Supporting Information**

489 Experimental details, optimised structures and chemical shifts of alkylammonium and
490 alkylamine chains, detailed optimisation results, energetic analysis of the relative
491 stability of different species, simulated infrared spectra of different species, root-mean-
492 square error of ^{15}N chemical shift calculation and three-dimensional structure of the
493 glycine cluster used to model the crystal structure of α -glycine. The Supporting
494 Information is available free of charge on the ACS Publications website at DOI:
495 10.1021/ ...

496

497

498 References

499

- 500 1. Leal, O.; Bolivar, C.; Sepúlveda, G.; Molleja, G.; Martínez, G.; Esparragoza, L. Carbon
501 Dioxide Adsorbent and Method for Producing the Adsorbent. U.S. Patent 5087597, 1992.
- 502 2. Leal, O.; Bolivar, C.; Ovalles, C.; Garcia, J. J.; Espidel, Y., Reversible adsorption of carbon
503 dioxide on amine surface-bonded silica gel. *Inorg. Chim. Acta* **1995**, *240*, 183-189.
- 504 3. Satyapal, S.; Filburn, T.; Trela, J.; Strange, J., Performance and Properties of a Solid
505 Amine Sorbent for Carbon Dioxide Removal in Space Life Support Applications. *Energy Fuels*
506 **2001**, *15*, 250-255.
- 507 4. Xu, X.; Song, C.; Andresen, J. M.; Miller, B. G.; Scaroni, A. W., Novel Polyethylenimine-
508 Modified Mesoporous Molecular Sieve of MCM-41 Type as High-Capacity Adsorbent for CO2
509 Capture. *Energy Fuels* **2002**, *16*, 1463-1469.
- 510 5. Younas, M.; Sohail, M.; Kong, L. L.; Bashir, M. J. K.; Sethupathi, S., Feasibility of CO2
511 adsorption by solid adsorbents: a review on low-temperature systems. *Int. J. Environ. Sci.*
512 *Technol.* **2016**, *13*, 1839-1860.
- 513 6. Wang, J.; Huang, L.; Yang, R.; Zhang, Z.; Wu, J.; Gao, Y.; Wang, Q.; O'Hare, D.; Zhong,
514 Z., Recent advances in solid sorbents for CO2 capture and new development trends. *Energy*
515 *Environ. Sci.* **2014**, *7*, 3478-3518.
- 516 7. Chen, C.; Zhang, S.; Row, K. H.; Ahn, W.-S., Amine-silica composites for CO2 capture:
517 A short review. *J. Energy Chem.* **2017**, *26*, 868-880.
- 518 8. Sanz-Pérez, E. S.; Murdock, C. R.; Didas, S. A.; Jones, C. W., Direct Capture of CO2 from
519 Ambient Air. *Chem. Rev.* **2016**, *116*, 11840-11876.
- 520 9. Gebald, C.; Repond, N.; Wurzbacher, J. A. Steam Assisted Vacuum Desorption Process
521 for Carbon Dioxide Capture. U.S. Patent 0203249 A1, 2017.
- 522 10. Gebald, C.; Meier, W.; Repond, N.; Ruesch, T.; Wurzbacher, J. A. Direct Air Capture
523 Device. U.S. Patent 0106330 A1, 2017.
- 524 11. Choi, S.; Drese, J. H.; Chance, R. R.; Eisenberger, P. M.; Jones, C. W. Application of
525 Amine-Tethered Solid Sorbents to CO2 Fixation from Air. U.S. Patent 8491705 B2, 2013.
- 526 12. Eisenberger, P. System and Method for Carbon Dioxide Capture and Sequestration.
527 U.S. Patent 8500855 B2, 2013.
- 528 13. Bhattacharyya, D.; Miller, D. C., Post-combustion CO2 capture technologies — a
529 review of processes for solvent-based and sorbent-based CO2 capture. *Curr. Opin. Chem. Eng.*
530 **2017**, *17*, 78-92.
- 531 14. Modak, A.; Jana, S., Advancement in porous adsorbents for post-combustion CO2
532 capture. *Micropor. Mesopor. Mater.* **2019**, *276*, 107-132.
- 533 15. Zhao, X.; Cui, Q.; Wang, B.; Yan, X.; Singh, S.; Zhang, F.; Gao, X.; Li, Y., Recent progress
534 of amine modified sorbents for capturing CO2 from flue gas. *Chin. J. Chem. Eng.* **2018**, *26*,
535 2292-2302.
- 536 16. Zhang, G.; Zhao, P.; Xu, Y.; Yang, Z.; Cheng, H.; Zhang, Y., Structure Property-CO2
537 Capture Performance Relations of Amine-Functionalized Porous Silica Composite Adsorbents.
538 *ACS Appl. Mater. Interfaces* **2018**, *10*, 34340-34354.
- 539 17. Chang, A. C. C.; Chuang, S. S. C.; Gray, M.; Soong, Y., In-Situ Infrared Study of CO2
540 Adsorption on SBA-15 Grafted with γ -(Aminopropyl)triethoxysilane. *Energy Fuels* **2003**, *17*,
541 468-473.

- 542 18. Khatri, R. A.; Chuang, S. S. C.; Soong, Y.; Gray, M., Carbon Dioxide Capture by Diamine-
543 Grafted SBA-15: A Combined Fourier Transform Infrared and Mass Spectrometry Study. *Ind.*
544 *Eng. Chem. Res.* **2005**, *44*, 3702-3708.
- 545 19. Hiyoshi, N.; Yogo, K.; Yashima, T., Adsorption characteristics of carbon dioxide on
546 organically functionalized SBA-15. *Micropor. Mesopor. Mater.* **2005**, *84*, 357-365.
- 547 20. Khatri, R. A.; Chuang, S. S. C.; Soong, Y.; Gray, M., Thermal and Chemical Stability of
548 Regenerable Solid Amine Sorbent for CO₂ Capture. *Energy Fuels* **2006**, *20*, 1514-1520.
- 549 21. Knöfel, C.; Martin, C.; Hornebecq, V.; Llewellyn, P. L., Study of Carbon Dioxide
550 Adsorption on Mesoporous Aminopropylsilane-Functionalized Silica and Titania Combining
551 Microcalorimetry and in Situ Infrared Spectroscopy. *J. Phys. Chem. C* **2009**, *113*, 21726-21734.
- 552 22. Sayari, A.; Belmabkhout, Y., Stabilization of Amine-Containing CO₂ Adsorbents:
553 Dramatic Effect of Water Vapor. *J. Am. Chem. Soc.* **2010**, *132*, 6312-6314.
- 554 23. Danon, A.; Stair, P. C.; Weitz, E., FTIR Study of CO₂ Adsorption on Amine-Grafted SBA-
555 15: Elucidation of Adsorbed Species. *J. Phys. Chem. C* **2011**, *115*, 11540-11549.
- 556 24. Bacsik, Z.; Ahlsten, N.; Ziadi, A.; Zhao, G.; Garcia-Bennett, A. E.; Martín-Matute, B. e.;
557 Hedin, N., Mechanisms and Kinetics for Sorption of CO₂ on Bicontinuous Mesoporous Silica
558 Modified with n-Propylamine. *Langmuir* **2011**, *27*, 11118-11128.
- 559 25. Pinto, M. L.; Mafra, L. s.; Guil, J. M.; Pires, J.; Rocha, J., Adsorption and Activation of
560 CO₂ by Amine-Modified Nanoporous Materials Studied by Solid-State NMR and ¹³CO₂
561 Adsorption. *Chem. Mater.* **2011**, *23*, 1387-1395.
- 562 26. Bollini, P.; Didas, S. A.; Jones, C. W., Amine-oxide hybrid materials for acid gas
563 separations. *J. Mater. Chem.* **2011**, *21*, 15100-15120.
- 564 27. Sayari, A.; Belmabkhout, Y.; Da'na, E., CO₂ Deactivation of Supported Amines: Does
565 the Nature of Amine Matter? *Langmuir* **2012**, *28*, 4241-4247.
- 566 28. Sayari, A.; Heydari-Gorji, A.; Yang, Y., CO₂-Induced Degradation of Amine-Containing
567 Adsorbents: Reaction Products and Pathways. *J. Am. Chem. Soc.* **2012**, *134*, 13834-13842.
- 568 29. Didas, S. A.; Sakwa-Novak, M. A.; Foo, G. S.; Sievers, C.; Jones, C. W., Effect of Amine
569 Surface Coverage on the Co-Adsorption of CO₂ and Water: Spectral Deconvolution of
570 Adsorbed Species. *J. Phys. Chem. Lett.* **2014**, *5*, 4194-4200.
- 571 30. Moore, J. K.; Sakwa-Novak, M. A.; Chaikittisilp, W.; Mehta, A. K.; Conradi, M. S.; Jones,
572 C. W.; Hayes, S. E., Characterization of a Mixture of CO₂ Adsorption Products in
573 Hyperbranched Aminosilica Adsorbents by ¹³C Solid-State NMR. *Environ. Sci. Technol.* **2015**,
574 *49*, 13684-13691.
- 575 31. Hahn, M. W.; Jelic, J.; Berger, E.; Reuter, K.; Jentys, A.; Lercher, J. A., Role of Amine
576 Functionality for CO₂ Chemisorption on Silica. *J. Phys. Chem. B* **2016**, *120*, 1988-1995.
- 577 32. Mafra, L.; Čendak, T.; Schneider, S.; Wiper, P. V.; Pires, J.; Gomes, J. R. B.; Pinto, M. L.,
578 Structure of Chemisorbed CO₂ Species in Amine-Functionalized Mesoporous Silicas Studied
579 by Solid-State NMR and Computer Modeling. *J. Am. Chem. Soc.* **2017**, *139*, 389-408.
- 580 33. Foo, G. S.; Lee, J. J.; Chen, C.-H.; Hayes, S. E.; Sievers, C.; Jones, C. W., Elucidation of
581 Surface Species through in Situ FTIR Spectroscopy of Carbon Dioxide Adsorption on Amine-
582 Grafted SBA-15. *Chem. Sus. Chem.* **2017**, *10*, 266-276.
- 583 34. Chen, C.-H.; Shimon, D.; Lee, J. J.; Didas, S. A.; Mehta, A. K.; Sievers, C.; Jones, C. W.;
584 Hayes, S. E., Spectroscopic Characterization of Adsorbed ¹³CO₂ on 3-Aminopropylsilyl-
585 Modified SBA15 Mesoporous Silica. *Environ. Sci. Technol.* **2017**, *51*, 6553-6559.
- 586 35. Shimon, D.; Chen, C.-H.; Lee, J. J.; Didas, S. A.; Sievers, C.; Jones, C. W.; Hayes, S. E.,
587 ¹⁵N Solid State NMR Spectroscopic Study of Surface Amine Groups for Carbon Capture: 3-

588 Aminopropylsilyl Grafted to SBA-15 Mesoporous Silica. *Environ. Sci. Technol.* **2018**, *52*, 1488-
589 1495.

590 36. Wang, X.; Schwartz, V.; Clark, J. C.; Ma, X.; Overbury, S. H.; Xu, X.; Song, C., Infrared
591 Study of CO₂ Sorption over “Molecular Basket” Sorbent Consisting of Polyethylenimine-
592 Modified Mesoporous Molecular Sieve. *J. Phys. Chem. C* **2009**, *113*, 7260-7268.

593 37. Yu, J.; Chuang, S. S. C., The Structure of Adsorbed Species on Immobilized Amines in
594 CO₂ Capture: An in Situ IR Study. *Energy Fuels* **2016**, *30*, 7579-7587.

595 38. Zhang, H.; Goepfert, A.; Olah, G. A.; Prakash, G. K. S., Remarkable effect of moisture
596 on the CO₂ adsorption of nano-silica supported linear and branched polyethylenimine. *J. CO₂*
597 *Utilization* **2017**, *19*, 91-99.

598 39. Bernin, D.; Hedin, N., Perspectives on NMR studies of CO₂ adsorption. *Curr. Opin.*
599 *Colloid Interface Sci.* **2018**, *33*, 53-62.

600 40. Young, P. D.; Notestein, J. M., The Role of Amine Surface Density in Carbon Dioxide
601 Adsorption on Functionalized Mixed Oxide Surfaces. *Chem. Sus. Chem.* **2011**, *4*, 1671-1678.

602 41. Mello, M. I. R.; Phanon, D.; Silveira, G. Q.; Llewellyn, P. L.; Ronconi, C. I. M., Amine-
603 modified MCM-41 mesoporous silica for carbon dioxide capture. *Micropor. Mesopor. Mater.*
604 **2011**, *143*, 174-179.

605 42. Huang, S.-J.; Hung, C.-T.; Zheng, A.; Lin, J.-S.; Yang, C.-F.; Chang, Y.-C.; Deng, F.; Liu, S.-
606 B., Capturing the Local Adsorption Structures of Carbon Dioxide in Polyamine-Impregnated
607 Mesoporous Silica Adsorbents. *J. Phys. Chem. Lett.* **2014**, *5*, 3183-3187.

608 43. Santos, T. C. d.; Bourrelly, S.; Llewellyn, P. L.; Carneiro, J. W. d. M.; Ronconi, C. M.,
609 Adsorption of CO₂ on amine-functionalised MCM-41: experimental and theoretical studies.
610 *Phys. Chem. Chem. Phys.* **2015**, *17*, 11095-11102.

611 44. Hung, C.-T.; Yang, C.-F.; Lin, J.-S.; Huang, S.-J.; Chang, Y.-C.; Liu, S.-B., Capture of carbon
612 dioxide by polyamine-immobilized mesostructured silica: A solid-state NMR study. *Micropor.*
613 *Mesopor. Mater.* **2017**, *238*, 2-13.

614 45. Milner, P. J.; Siegelman, R. L.; Forse, A. C.; Gonzalez, M. I.; Runcěvski, T.; Martell, J. D.;
615 Reimer, J. A.; Long, J. R., A Diaminopropane-Appended Metal–Organic Framework Enabling
616 Efficient CO₂ Capture from Coal Flue Gas via a Mixed Adsorption Mechanism. *J. Am. Chem.*
617 *Soc.* **2017**, *139*, 13541-13553.

618 46. Lee, J. J.; Chen, C.-H.; Shimon, D.; Hayes, S. E.; Sievers, C.; Jones, C. W., Effect of
619 Humidity on the CO₂ Adsorption of Tertiary Amine Grafted SBA-15. *J. Phys. Chem. C* **2017**,
620 *121*, 23480-23487.

621 47. Čendak, T.; Sequeira, L.; Sardo, M.; Valente, A.; Pinto, M. s. L.; Mafra, L. s., Detecting
622 proton-transfer in CO₂ species chemisorbed on amine- modified mesoporous silicas using ¹³C
623 NMR chemical shift anisotropy and smart control of amine surface density. *Chem. Eur. J.* **2018**,
624 *24*, 10136-10145.

625 48. Moschetta, E. G.; Sakwa-Novak, M. A.; Greenfield, J. L.; Jones, C. W., Post-Grafting
626 Amination of Alkyl Halide-Functionalized Silica for Applications in Catalysis, Adsorption, and
627 ¹⁵N NMR Spectroscopy. *Langmuir* **2015**, *31*, 2218-2227.

628 49. Mafra, L.; Čendak, T.; Schneider, S.; Wiper, P. V.; Pires, J. o.; Gomes, J. R. B.; Pinto, M.
629 s. L., Amine functionalized porous silica for CO₂/CH₄ separation by adsorption: Which amine
630 and why. *Chem. Eng. J.* **2018**, *336*, 612-621.

631 50. Choi, M.; Kleitz, F.; Liu, D.; Lee, H. Y.; Ahn, W.-S.; Ryoo, R., Controlled Polymerization
632 in Mesoporous Silica toward the Design of Organic-Inorganic Composite Nanoporous
633 Materials. *J. Am. Chem. Soc.* **2005**, *127*, 1924-1932.

634 51. Samultsev, D. O.; Semenov, V. A.; Krivdin, L. B., On the accuracy of the GIAO-DFT
635 calculation of ¹⁵N NMR chemical shifts of the nitrogen- containing heterocycles – a gateway
636 to better agreement with experiment at lower computational cost. *Magn. Reson. Chem.* **2014**,
637 *52*, 222-230.

638 52. Chapyshev, S. V.; Ushakov, E. N.; Chernyak, A. V., ¹⁵N NMR spectra and reactivity of
639 2,4,6- triazidopyridines, 2,4,6-triazidopyrimidine and 2,4,6-triazido-s-triazine. *Magn. Reson.*
640 *Chem.* **2013**, *51*, 562-568.

641 53. Chapyshev, S. V.; Chernyak, A. V.; Ushakov, E. N., ¹³C and ¹⁵N NMR spectra of high-
642 energy polyazidocyanopyridines. *Magn. Reson. Chem.* **2016**, *55*, 99-105.

643 54. Mouline, Z.; Asai, K.; Daiko, Y.; Honda, S.; Bernard, S.; Iwamoto, Y., Amine-
644 functionalized polycarbosilane hybrids for CO₂-selective membranes. *J. Eur. Ceram. Soc.*
645 **2017**, *37*, 5213-5221.

646 55. Stefanovich, E. V.; Boldyrev, A. I.; Truong, T. N.; Simons, J., Ab Initio Study of the
647 Stabilization of Multiply Charged Anions in Water. *J. Phys. Chem. B* **1998**, *201*, 4205-4208.

648 56. Adams, J. M.; Small, R. W. H., The crystal structure of ammonium carbamate. *Acta*
649 *Crystallogr., Sect. B: Struct. Sci. Cryst. Eng. Mater.* **1973**, *29*, 2317-2319.

650 57. Bracher, B. H.; Small, R. W. H., The crystal structure of ethyl carbamate. *Acta Cryst.*
651 **1967**, *23*, 410-418.

652 58. Cañellas, S.; Ayats, C.; Henseler, A. H.; Pericàs, M. A., CCDC 1577682: Experimental
653 Crystal Structure Determination. **2017**.

654 59. Ma, Z.; Day, C. S.; Bierbach, U., CCDC 657432: Experimental Crystal Structure
655 Determination. 2014.

656 60. Pesenti, C.; Bravo, P.; Corradi, E.; Frigerio, M.; Meille, S. V.; Panzeri, W.; Viani, F.;
657 Zanda, M., CCDC 176640: Experimental Crystal Structure Determination. **2014**.

658 61. Siwicka, A.; Moleda, Z.; Wojtasiewicz, K.; Zawadzka, A.; Maurin, J. K.; Panasiewicz, M.;
659 Pacuszk, T.; Czarnocki, Z., CCDC 667929: Experimental Crystal Structure Determination.
660 2014.

661 62. Aziz, B.; Zhao, G.; Hedin, N., Carbon Dioxide Sorbents with Propylamine Groups-Silica
662 Functionalized with a Fractional Factorial Design Approach. *Langmuir* **2011**, *27*, 3822-3834.

663 63. Aziz, B.; Hedin, N.; Bacsik, Z., Quantification of chemisorption and physisorption of
664 carbon dioxide on porous silica modified by propylamines: Effect of amine density. *Micropor.*
665 *Mesopor. Mater.* **2012**, *159*, 42-49.

666 64. Tumuluri, U.; Isenberg, M.; Tan, C.-S.; Chuang, S. S. C., In Situ Infrared Study of the
667 Effect of Amine Density on the Nature of Adsorbed CO₂ on Amine-Functionalized Solid
668 Sorbents. *Langmuir* **2014**, *30*, 7405-7413.

669 65. Potter, M. E.; Cho, K. M.; Lee, J. J.; Jones, C. W., Role of Alumina Basicity in CO₂ Uptake
670 in 3-Aminopropylsilyl-grafted Alumina Adsorbents. *Chem. Sus. Chem.* **2017**, *10*, 2192-2201.

671 66. Bacsik, Z.; Atluri, R.; Garcia-Bennett, A. E.; Hedin, N., Temperature-Induced Uptake of
672 CO₂ and Formation of Carbamates in Mesocaged Silica Modified with n-Propylamines.
673 *Langmuir* **2010**, *26*, 10013-10024.

674 67. Huang, H. Y.; Yang, R. T.; Chinn, D.; Munson, C. L., Amine-Grafted MCM-48 and Silica
675 Xerogel as Superior Sorbents for Acidic Gas Removal from Natural Gas. *Ind. Eng. Chem. Res.*
676 **2003**, *42*, 2427-2433.

677 68. Serna-Guerrero, R.; Da'na, E.; Sayari, A., New Insights into the Interactions of CO₂ with
678 Amine-Functionalized Silica. *Ind. Eng. Chem. Res.* **2008**, *47*, 9406-9412.

679 69. Zelenak, V.; Halamova, D.; Gaberova, L.; Bloch, E.; Llewellyn, P., Amine-modified SBA-
680 12 mesoporous silica for carbon dioxide capture: Effect of amine basicity on sorption
681 properties. *Micropor. Mesopor. Mater.* **2008**, *116*, 358-364.

682 70. Hiyoshi, N.; Yogo, K.; Yashima, T., Reversible Adsorption of Carbon Dioxide on Amine-
683 Modified SBA-15 from Flue Gas Containing Water Vapor. *Stud. Surf. Sci. Catal.* **2004**, *153*, 417-
684 422.

685 71. Bacsik, Z.; Hedin, N., Effects of carbon dioxide captured from ambient air on the
686 infrared spectra of supported amines. *Vib. Spectrosc.* **2016**, *87*, 215-221.

687 72. Xu, X.; Song, C.; Miller, B. G.; Scaroni, A. W., Influence of Moisture on CO₂ Separation
688 from Gas Mixture by a Nanoporous Adsorbent Based on Polyethylenimine-Modified
689 Molecular Sieve MCM-41. *Ind. Eng. Chem. Res.* **2005**, *44*, 8113-8119.

690 73. Belmabkhout, Y.; Serna-Guerrero, R.; Sayari, A., Amine-bearing mesoporous silica for
691 CO₂ removal from dry and humid air. *Chem. Eng. Sci.* **2010**, *65*, 3695-3698.

692 74. Goepfert, A.; Czaun, M.; May, R. B.; Prakash, G. K. S.; Olah, G. A.; Narayanan, S. R.,
693 Carbon Dioxide Capture from the Air Using a Polyamine Based Regenerable Solid Adsorbent.
694 *J. Am. Chem. Soc.* **2011**, *133*, 20164-20167.

695 75. Hiyoshi, N.; Yogo, K.; Yashima, T., Adsorption of Carbon Dioxide on Amine Modified
696 SBA-15 in the Presence of Water Vapor. *Chem. Lett.* **2004**, *33*, 510-511.

697 76. Knowles, G. P.; Graham, J. V.; Delaney, S. W.; Chaffee, A. L., Aminopropyl-
698 functionalized mesoporous silicas as CO₂ adsorbents. *Fuel Process. Technol.* **2005**, *86*, 1435-
699 1448.

700 77. Knowles, G. P.; Delaney, S. W.; Chaffee, A. L., Diethylenetriamine[propyl(silyl)]-
701 Functionalized (DT) Mesoporous Silicas as CO₂ Adsorbents. *Ind. Eng. Chem. Res.* **2006**, *45*,
702 2626-2633.

703