

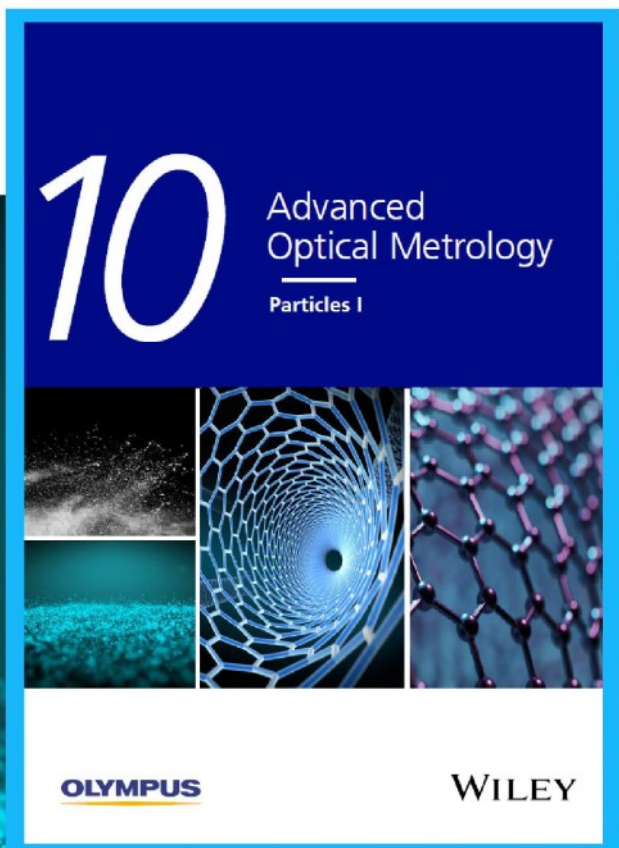


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# Great Location: About Effects of Surface Bound Neighboring Groups for Passive and Active Fine-Tuning of CO<sub>2</sub> Adsorption Properties in Model Carbon Capture Materials

Nele Klinkenberg, Sophia Kraft, and Sebastian Polarz\*


Improved carbon capture materials are crucial for managing the CO<sub>2</sub> level in the atmosphere. The past focus was on increasing adsorption capacities. It is widely known that controlling the heat of adsorption ( $\Delta H_{\text{ads}}$ ) is equally important. If it is too low, CO<sub>2</sub> uptake takes place at unfavorable conditions and with insufficient selectivity. If it is too high, chemisorption occurs, and the materials can hardly be regenerated. The conventional approach for influencing  $\Delta H_{\text{ads}}$  is the modification of the adsorbing center. This paper proposes an alternative strategy. The hypothesis is that fine-tuning of the molecular environment around the adsorbing center is a powerful tool for the adjustment of CO<sub>2</sub>-binding properties. Via click chemistry, any desired neighboring group (NG) can be incorporated on the surfaces of the nanoporous organosilica model materials. Passive NGs induce a change in the polarity of the surface, whereas active NGs are capable of direct interaction with the active center/CO<sub>2</sub> pair. The effects on  $\Delta H_{\text{ads}}$  and on the selectivity are studied. A situation can be realized which resembles frustrated Lewis acid–base pairs, and the investigation of the binding-species by solid-state NMR indicates that the push–pull effects could play an essential role not only in CO<sub>2</sub> adsorption but also in its activation.

Carbon capture materials (CCMs) represent one building block to tackle today's challenges regarding climate change. Key applications are the reduction of CO<sub>2</sub> emissions and the removal of CO<sub>2</sub> from biogas/natural gas to permit its use and transportation. Furthermore, direct air capture systems are extensively researched that would allow the effective reduction of the atmospheric

concentration.<sup>[1]</sup> Over the last few years, numerous materials such as porous silica, metal-organic frameworks (MOFs), zeolites, porous carbons, covalent organic/triazine frameworks (COFs/CTFs) and porous organic polymers (POPs) have been proposed for carbon capture applications.<sup>[1b,2]</sup> Within these materials, chemical adsorbents play an important role as they offer an increased affinity towards CO<sub>2</sub>, which is essential for the application of CCMs in diluted applications.<sup>[1a,3]</sup> Ideally, CCMs should combine a high capacity, high affinity but easy regeneration, high selectivity, and tolerance against impurities as, e.g., water and other trace gases.<sup>[1a,4]</sup> However, the perfect material to meet all these criteria has not been found yet. Model systems can be used to identify the most important design principles to improve the performance of future CCMs. One key challenge for the design of next-generation chemical adsorbents is finding the ideal balance between heat of adsorption  $\Delta H_{\text{ads}} \leftrightarrow$  regeneration energy and selectivity.<sup>[1a]</sup> So far, two main strategies exist to optimize these metrics of CCMs: optimization of the active capturing center and optimization of the porous structure.

Herein, we propose a new strategy: changing the molecular environment in direct vicinity to the adsorbing center to influence CO<sub>2</sub> adsorption. Our hypothesis is that the interaction of the active capturing group (e.g., amine, –NH<sub>2</sub>) with CO<sub>2</sub> can be modulated via the introduction of different functional groups present in the direct neighborhood. First hints exist in literature that, in fact, the nanoenvironment plays an important role in chemical CO<sub>2</sub> adsorption processes. Amine-functionalized materials are a widely studied class of CCMs.<sup>[5]</sup> Mechanistic studies revealed that neighboring groups (NGs), adjacent amine groups on the surface, for example, influence the CO<sub>2</sub> adsorption.<sup>[5a,c,6]</sup> It has been reported that also silanol groups (SiOH), present in silica materials, have an effect.<sup>[5a,6a–d]</sup> Different surface-bound species have been identified via IR and NMR spectroscopy, such as the most commonly discussed carbamate,<sup>[5a,c,6]</sup> but also urea<sup>[6b,e]</sup> or bicarbonate species.<sup>[6e,f]</sup> So far, only few studies have focused on the influence of neighboring groups. Wang et al. studied the influence of coexisting pyridinic nitrogen species with adjacent OH/NH<sub>2</sub> species and found that these neighboring groups play an important role in enhancing the capture performance

N. Klinkenberg, S. Kraft, Prof. S. Polarz  
Department of Chemistry  
University of Konstanz  
Universitätsstr. 10, Konstanz 78464, Germany  
E-mail: sebastian.polarz@aca.uni-hannover.de  
Prof. S. Polarz  
Institute of Inorganic Chemistry  
Leibniz University Hannover  
Callinstr. 9, Hannover 30167, Germany

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.202007734>.

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of porous organic polymers.<sup>[7]</sup> Bloch et al. showed a first example of NG interactions with other functional groups.<sup>[8]</sup> They used an indole carrying a second functional group to investigate the interplay between the secondary amine of the indole and the second functional group.

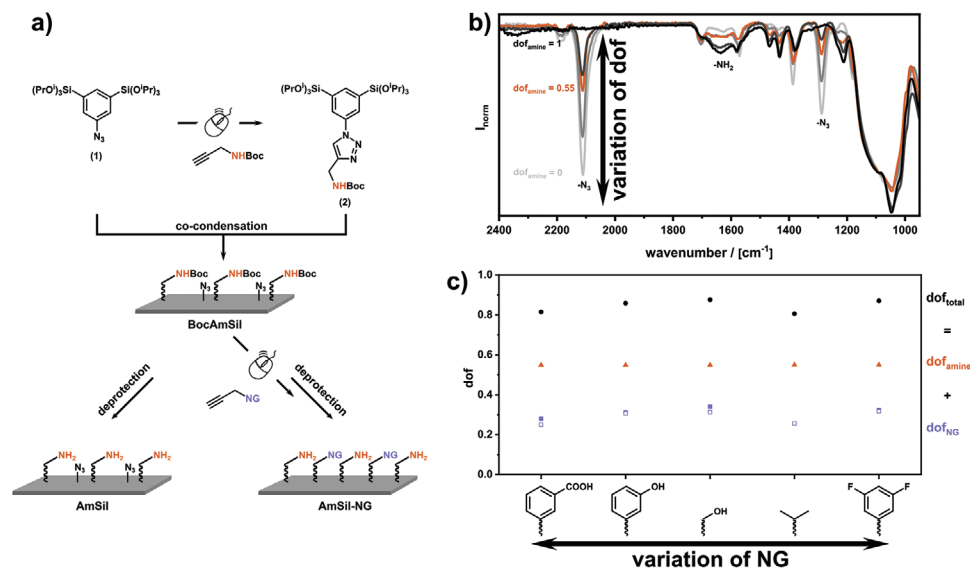
One reason there is a lack of studies on NG effects is that suitable model adsorbents need to fulfill a complex set of criteria. The independent introduction of two different functional groups should be possible (1), with preferably no restriction regarding the type of functional groups (2). One needs control over the density of those groups in the materials (3). The influence of the variation in functionalization on the material's structure should be minimal to ensure comparability between different sets of data (4). The surface area needs to be high enough to enable investigation via volumetric adsorption techniques (5). Observed effects should be dominated by thermodynamic and not kinetic factors (6).

Based on our extensive experience in porous organosilica materials,<sup>[9]</sup> which can be modified by click chemistry, we can now realize all of the requirements for model materials formulated above and, therefore, pave the way for a systematic exploration of NG effects. The target organosilica model material(s) can be achieved by a combined cocondensation/postfunctionalization click chemistry strategy as shown in Figure 1a. The new aminated sol-gel precursor compound (2) was obtained from (1) via the 1,3-dipolar Huisgen cycloaddition reaction as described in detail in the experimental section (see Supporting Information), and is thoroughly characterized by <sup>1</sup>H-, <sup>13</sup>C-, and <sup>29</sup>Si-NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS) (see Figure S1 in the Supporting Information). It should be noted, the amine is protected by a butoxy (boc), because we want to avoid that the basic character of the free -NH<sub>2</sub> has any unwanted effects on the subsequent sol-gel process. Material(s)

containing the primary amines as the active centers for CO<sub>2</sub> binding can then be obtained by deprotection (Figure 1a).

Previous studies in our group showed that cocondensation of arbitrary ratios of bridged silsesquioxanes leads to bifunctional materials with a statistical distribution of functional groups on the nanoscale.<sup>[10]</sup> Therefore, the use of the known phenylazide-bridged precursor (1)<sup>[9b]</sup> together with (2) ensures a homogeneous and defined "background" of primary amine groups on the surface of the planned porous materials. The latter is demonstrated in Figure 1b. Materials with degrees of functionalization (dof) ranging from 0 (only AzPrec(1)) to 1 (only BocAmPrec(2)) have been prepared. The dof can be monitored by the intensity of the asymmetric azide vibration at 2112 cm<sup>-1</sup> after normalizing the spectra to the Si-O-Si band at ≈1000–1200 cm<sup>-1</sup> (for details see Figure S3 and Table S1 in the Supporting Information). The azide vibrations (vib<sub>asym</sub> = 2112 cm<sup>-1</sup> and vib<sub>sym</sub> = 1288 cm<sup>-1</sup>) become weaker with increasing amine functionalization (dof<sub>amine</sub> → 1), and vice-versa considering the amine deformation vibration at 1635 cm<sup>-1</sup> (Figure 1b). The homogeneity of the "amine background" on the micrometer scale can be proven by IR microscopy (Figure S2, Supporting Information), as the intensity of the azide vibration and, thus, also the amine concentration does not vary over several hundred micrometers.

The NGs are introduced in the second step via click chemistry postfunctionalization as shown in Figure 1a. Any functional group can be incorporated, which is available with an alkyne linker attached to it. The selection realized here is shown in Figure 1c. For proof of concept, the amine content was set at dof<sub>amine</sub> = 0.55. Ideally, the number of azide groups (dof<sub>azide</sub> = 1 - dof<sub>amine</sub>) also determines the amount of neighboring groups. In reality, dof<sub>NG</sub> can be smaller, if not all



**Figure 1.** a) Material synthesis of monofunctional AmSil and bifunctional AmSil-NG materials. b) IR spectra of AmSil materials synthesized with varying ratios of precursors (1) and (2). Dofs from 0 (light gray, pure AzPrec (1)) to 1 (black, pure BocAmPrec (2)) can be obtained. For further functionalization with NGs, AmSil with dof<sub>amine</sub> = 0.55 (orange) was used within this publication. c) Various neighboring groups can be introduced via postfunctionalization of BocAmSil. The dof<sub>total</sub> (black) of AmSil-NG materials is determined by IR spectroscopy. The dof<sub>amine</sub> (purple) corresponds to dof<sub>NG</sub> = dof<sub>total</sub> - dof<sub>amine</sub>. Dof<sub>amine</sub> (orange triangles) is given by the proportion of (2) used in the cocondensation. The dof<sub>NG</sub> is confirmed through TGA measurements (purple, open squares). For information on how to determine the dof from IR and TGA, respectively, see Table S1 (Supporting Information).

azide participate in the click reaction, e.g., because they are buried in the pore-wall. Residual azide groups can be determined from IR spectroscopy as shown above. It is deduced that 26–34% of the surface groups in the final materials are NGs (Figure 1c). Thermogravimetric analysis (TGA) was used as an independent method to confirm and quantify the success of the click modification (Figure 1c; see also Figure S4 and Table S1 in the Supporting Information).

For all further investigations, it is crucial that the amine groups are still intact and accessible after the introduction of the NG. The activity of the amine functionalities was checked by the Ninhydrin test shown in Figure S5 (Supporting Information). None of the materials contain copper as a potential impurity originating from the click catalyst as proven by energy-dispersive X-ray (EDX) spectroscopy (Figure S6, Supporting Information). It can be summarized that the criteria (1–3) formulated above are fulfilled.

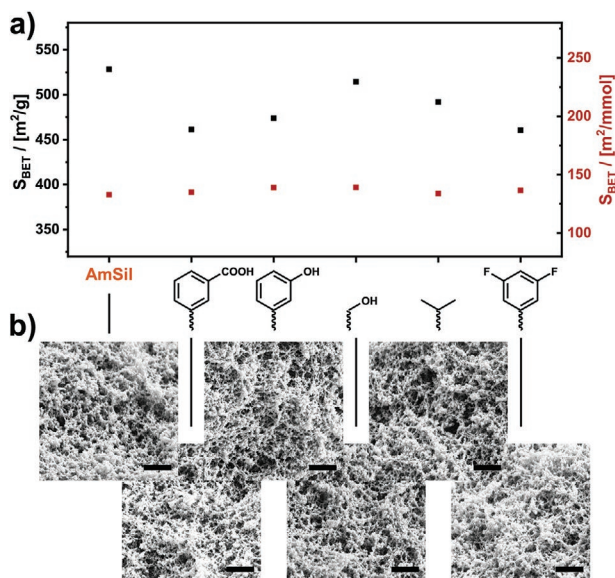
The fourth criterion for a suitable model system was that there are no substantial changes in the structure for materials containing different NGs. It is known that in general structure, surface area and pore size have a tremendous effect on the CO<sub>2</sub> uptake.<sup>[1a,2a,4,11]</sup> To focus on the specific chemical influence of the different NG, it is thus necessary to ensure minimal structural influence. For micropores, a decrease in surface area, pore diameter or even blocking of pores has been reported due to functionalization.<sup>[12]</sup> As sorption in micropores is especially sensible to the pore size,<sup>[2a,4]</sup> this could lead to overlay effects due to structural change, hiding the chemical effect caused by the NG.<sup>[2a,4]</sup> Therefore, meso-/macroporous aerogels were chosen herein. The structure of the prepared aerogels was characterized by scanning electron microscopy (SEM) and is shown in Figure 2b. There are no obvious morphological differences, no matter which NG was incorporated. The latter conclusion can be confirmed by N<sub>2</sub>-physisorption isotherms shown in Figure S7

(Supporting Information), which were also used to calculate the specific surface area  $S_{\text{BET}}$  of the materials (Figure 2a). Almost no gas is adsorbed at relative pressure  $p/p^0 < 0.1$ , which is the characteristic region for micropores. As stated before, their absence is an advantage, because this means that the planned CO<sub>2</sub> studies will not be influenced by sorption in micropores. Because the larger pores in aerogels are very well accessible, there is also less chance for the occurrence of kinetic phenomena during gas uptake that have been found in microporous materials.<sup>[1a,2a]</sup> The specific surface areas (460 to 528 m<sup>2</sup> g<sup>-1</sup>) are reasonably high for aerogels and sufficient for a model system for CO<sub>2</sub>, in particular, because we do not focus on high(est) uptake capacities. To ensure both criteria, minimal structural influence and minimal kinetic influence are met, the absence of micropores in our model systems are necessary, which results in lower capacities compared to state-of-the-art materials.

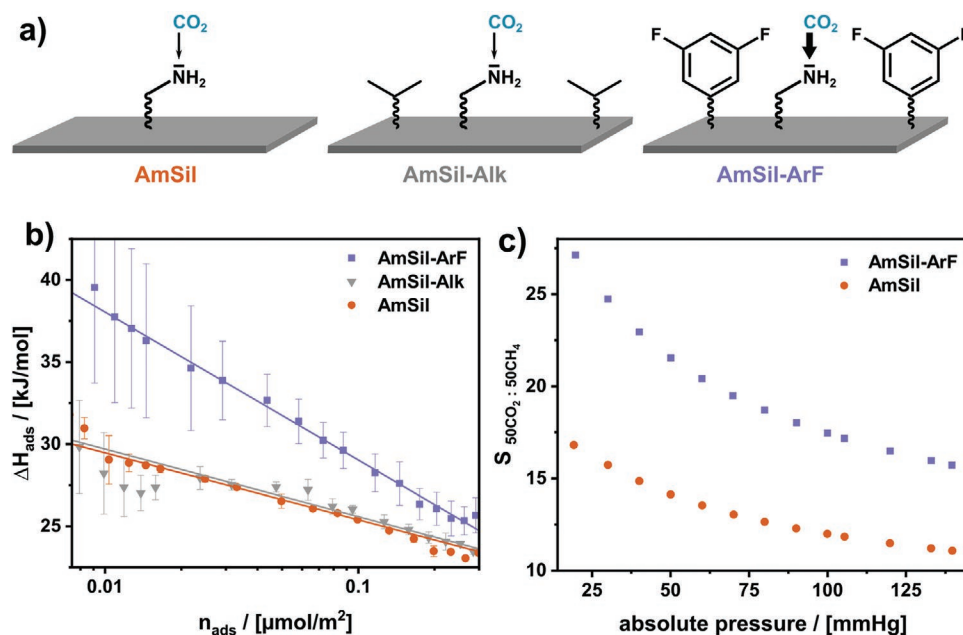
The density  $\rho$  of a material enters the surface area expressed in m<sup>2</sup> g<sup>-1</sup>. Because the molecular mass of the NGs is different in addition to a slightly different degree of functionalization (Figure 1c), the values for  $\rho$  are also not exactly the same. The latter factor explains why the materials seemingly deviate in surface area in (m<sup>2</sup> g<sup>-1</sup>). Therefore, it is better to convert  $S_{\text{BET}}$  to the unit m<sup>2</sup> mol<sup>-1</sup>. The necessary calculation is possible, because we know the composition and the molar masses of the material. One can see, that there are very minor changes when the materials contain a different NG.

Two key metrics for CCMs were chosen to test our hypothesis that NGs in direct vicinity to the adsorbing amine have a substantial impact on properties regarding CO<sub>2</sub> adsorption: the heat of adsorption ( $\Delta H_{\text{ads}}$ ) and the selectivity over CH<sub>4</sub>.  $\Delta H_{\text{ads}}$  was calculated using the Clausius-Clapeyron equation based on CO<sub>2</sub> isotherms at 30 °C, 40 °C, and 50 °C.<sup>[13]</sup> The CO<sub>2</sub>/CH<sub>4</sub> selectivity was determined from pure gas isotherms of CO<sub>2</sub> and CH<sub>4</sub> via the ideal adsorbed solution theory (IAST) developed by Myers and Prausnitz<sup>[14]</sup> with pyIAST.<sup>[15]</sup> The suitability of IAST to determine the selectivity of CO<sub>2</sub> over CH<sub>4</sub> has been shown by comparison to data from experimental<sup>[16]</sup> and simulated<sup>[17]</sup> co-adsorption for various materials. However, it should be noted that with special equipment, which is capable of differentiation of gases, it is possible to investigate a competitive adsorption scenario directly.<sup>[18]</sup> The selectivity is determined for a 50/50 mixture, as this is commonly used in literature as a test system for biogas applications as the CO<sub>2</sub> content in biogas can reach up to 50%.<sup>[3b]</sup> We differentiate two types of NGs. One type (passive) is not able to chemically interact neither with the amine nor with the CO<sub>2</sub>, thus, is not expected to influence the  $\Delta H_{\text{ads}}$  or the selectivity. The second type (active NGs) could possibly interact with the amine or with the CO<sub>2</sub>/amine adduct.

We start the discussion with two representatives for passive NGs (see Figure 3). Except for van der Waals forces, neither alkyl NGs nor bis-fluorinated benzene (ArF) NGs should interfere with the amine group on the surface. The formulated expectation is fulfilled, when we compare the NG-free AmSil with AmSil-Alk.  $\Delta H_{\text{ads}}$  is pressure-dependent, respectively decreases with increasing coverage of the surface with CO<sub>2</sub> groups, respectively correlates to the number of already adsorbed CO<sub>2</sub> molecules ( $n_{\text{ads}}$ ). The range  $\Delta H_{\text{ads}} = 35\text{--}20$  kJ mol<sup>-1</sup> for AmSil is at the edge between physisorption and chemisorption.<sup>[1a]</sup> It can be seen (Figure 3b) that the



**Figure 2.** a) BET surface area ( $S_{\text{BET}}$ ) of AmSil and AmSil-NG materials determined from N<sub>2</sub> physisorption measurements. Corresponding N<sub>2</sub> isotherms can be found in Figure S7 (Supporting Information). b) SEM micrographs of AmSil and AmSil-NG materials. Scale bar: 1 μm.



**Figure 3.** a) The influence of allegedly passive neighboring groups on the  $\text{CO}_2$  adsorption is investigated. b) Heat of adsorption ( $\Delta H_{ads}$ ) determined from  $\text{CO}_2$  isotherms at  $T = 30^\circ\text{C}$ ,  $40^\circ\text{C}$ , and  $50^\circ\text{C}$  of AmSil–ArF (purple squares), AmSil–Alk (gray triangles), and AmSil (orange circles). and c) IAST-selectivity at  $T = 30^\circ\text{C}$  for a 50:50 mixture of  $\text{CO}_2$  and  $\text{CH}_4$  of AmSil–ArF (purple squares) and AmSil (orange circles). Primary data can be found in Figure S9 (Supporting Information).

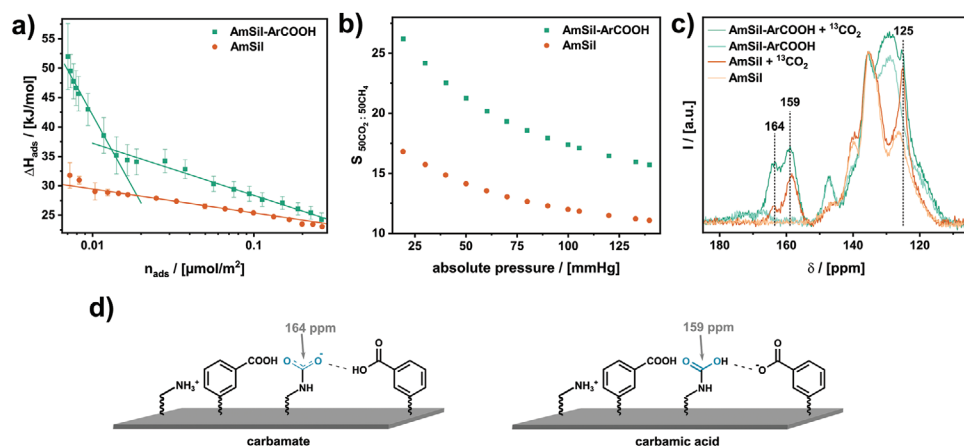
presence of isopropyl NGs on the surface has no effect on the  $\Delta H_{ads}(n_{\text{CO}_2})$  function.

AmSil–ArF clearly behaves differently. The  $\Delta H_{ads}$  values are significantly higher, which means adjacent ArF can increase the affinity of the amines towards  $\text{CO}_2$ . Consequently, one would also expect a significant effect on the selectivity of adsorption. One can see that the selectivity over  $\text{CH}_4$  is increased by up to 61% for AmSil–ArF (Figure 3c). It is remarkable that ArF is obviously much less passive, than we had expected. For a possible explanation, one can view the adsorption process as a nucleophilic attack of the lone-pair at the amine group on the electrophilic carbon atom in  $\text{CO}_2$ . The reactivity in second-order nucleophilic substitution reactions ( $\text{S}_{\text{N}2}$ ) depends, according to organic textbook knowledge, on the polarity of the solvent. The reactivity is much higher in apolar solvents. Furthermore, it is known that the introduction of fluorine atoms in organic compounds decreases the polarity, and surfaces modified by fluorinated constituents become hydrophobic. This can be shown also for AmSil–ArF, as the contact angle with water is significantly increased compared to AmSil without the NG (Figure S8, Supporting Information). Therefore, our conclusion is that the lone pair at the N-atom is more “naked”, when the local environment of the amine group on the surface is made less polar as a consequence of the presence of ArF as NGs. According to some reports in literature, there might be an additional, quadrupolar interaction between the C–F bond and  $\text{CO}_2$ .<sup>[19]</sup>

Benzoic acid appeared most attractive to us as an active NG. The conventional approach in CCMs is to increase the amine amount and thus the basicity of the material, which is why the introduction of an acidic NG is counter-intuitive. As an acid, it should be obstructive for a  $\text{CO}_2$ -capture material, but a surface

containing separated acid and base centers resembles frustrated acid-base pairs, which are known from molecular catalysis.<sup>[20]</sup> The  $\text{CO}_2$  adsorption studies were performed, treated as described above, and the results are plotted in Figure 4. The introduction of benzoic acid as a NG leads to a much more pronounced change/increase of  $\Delta H_{ads}$  compared to the allegedly passive ArF NG (Figure 4a). However, there is an additional and striking difference. Other than for the passive groups, there is a glitch in the  $\Delta H_{ads}(n_{\text{CO}_2})$  plot for the active NG case. This means that between  $n_{\text{CO}_2} = 0 - 0.014 \mu\text{mol m}^{-2}$  a chemically different adsorption site exists compared to the one at higher surface coverage, which becomes occupied at higher pressure.

$^{13}\text{C}$ -cross polarization (CP)-magic angle spinning (MAS)-NMR spectroscopy using  $^{13}\text{C}$ -labeled  $\text{CO}_2$  was conducted as a powerful tool for the identification of binding species.<sup>[6c,e,21]</sup> Figure 4c shows the  $^{13}\text{C}$ -CP-MAS-NMR spectra of AmSil–ArCOOH and AmSil before and after the addition of  $^{13}\text{CO}_2$ . While the peak at 125 ppm has been identified as physically adsorbed  $\text{CO}_2$ , the peaks at 159 ppm and 164 ppm are characteristic for chemically adsorbed  $\text{CO}_2$ .<sup>[6e,21]</sup> It can be seen that the addition of the NG in AmSil–ArCOOH leads to an overall increase in chemisorbed species as well as the promotion of the band at 164 ppm compared to AmSil without a NG. The main species at 159 ppm can be assigned to a carbamic acid binding species (Figure 4c).<sup>[21a]</sup> The chemical shift for the second species (164 ppm) indicates a carbamate-type species.<sup>[6c,e,21]</sup> Conventionally, in amine-functionalized materials, these carbamate species are stabilized by adjacent amine groups. However, because the amine density is identical for AmSil–ArCOOH and AmSil (Figure 1c), the promotion of that species in AmSil–ArCOOH cannot be attributed to a higher amount of amines. Therefore, the promotion of the species at



**Figure 4.** a)  $\Delta H_{\text{ads}}$  determined using  $\text{CO}_2$  isotherms at  $T = 30\text{ }^\circ\text{C}$ ,  $40\text{ }^\circ\text{C}$ , and  $50\text{ }^\circ\text{C}$  and b) IAST-selectivity at  $T = 30\text{ }^\circ\text{C}$  for a 50:50 mixture of  $\text{CO}_2$  and  $\text{CH}_4$  of AmSil–ArCOOH (green squares) and AmSil (orange circles). Primary data can be found in Figure S9 (Supporting Information). c)  $^{13}\text{C}$ -CP-MAS-NMR of AmSil–ArCOOH (green) and AmSil (orange) before (light color) and after (darker color) the addition of  $^{13}\text{CO}_2$ . Full spectrum can be found in Figure S10 (Supporting Information). d) Possible binding species in AmSil–ArCOOH identified via  $^{13}\text{C}$ -CP-MAS-NMR spectroscopy.

164 ppm in AmSil–ArCOOH has to be due to the incorporation of the benzoic acid NG. We propose a carbamate-type species that is stabilized by the benzoic acid NG (see Figure 4d). Carbamate species are known to be more stable than carbamic acid, which is in agreement with the higher  $\Delta H_{\text{ads}}$  of AmSil–ArCOOH compared to AmSil. Carbamate species stabilized by adjacent amine groups are reported to be stable under evacuation and can only be removed in combination with increased temperatures.<sup>[21a]</sup> However, in AmSil–ArCOOH, both species can be completely removed after evacuation for 3 h at room temperature (see Figure S10 in the Supporting Information) meaning that also the carbamate species found herein is labile. To confirm that the presented AmSil–NG materials can be regenerated in vacuo, cyclic adsorption–desorption measurements were performed (Figure S11, Supporting Information) as an alternative to pressure swing adsorption measurements.<sup>[22]</sup> The capacity stays constant over multiple cycles under isothermal conditions and no increase in temperature is necessary to regenerate the AmSil–NG materials. Pinto et al. stated that such labile chemisorbed species are desired to catalyze the activation of  $\text{CO}_2$ , as the instability of the adsorbed species consequently leads to a higher reactivity in the consequent reaction.<sup>[21a]</sup> Thus, they suggested the maximization of labile chemisorbed species such as carbamic acid to achieve higher reactivity. By using a benzoic acid NG in AmSil–ArCOOH, we could not only increase the formation of carbamic acid, but also a second carbamate-type species is promoted that is less stable compared to conventional carbamate species. This demonstrates that using NGs to influence the nanoenvironment of amine species in amine-functionalized materials represents a highly promising strategy for material design in  $\text{CO}_2$  activation applications.

This work underlines the vast opportunities that open up by tailoring the molecular environment in direct vicinity to the adsorbing amine to influence the interaction with  $\text{CO}_2$ . The investigation of these NG effects was enabled by establishing a new, highly flexible synthesis strategy to bifunctional model systems. The degree of functionalization as well as the functional group can be varied, while the structure is preserved. The

investigation of allegedly passive NGs revealed that even groups that are not able to chemically interact with the adsorbing amine or  $\text{CO}_2$  can already distinctly influence the  $\text{CO}_2$  adsorption. The introduction of an active NG, leading to the combination of a basic amine with an acidic NG resulted in even more interesting effects. While the  $\Delta H_{\text{ads}}$  could be increased by up to 64%, the chemisorbed species identified via  $^{13}\text{C}$ -CP-MAS-NMR with  $^{13}\text{CO}_2$  could be removed in vacuo. Such chemically adsorbed, but labile species are highly interesting for  $\text{CO}_2$  activation. Tailoring the nanoenvironment of CCMs thus represents a new strategy that could lead to next-generation CCMs for  $\text{CO}_2$  adsorption and activation. In future research, it would be interesting to transfer the herein identified NG-amine motifs to materials with smaller pores and even higher surface areas such as, e.g., periodic mesoporous organosilica (PMOs) or MOFs to further increase capacity and selectivity. Furthermore, it is known that the presence of water is another factor, which could influence the adsorption of  $\text{CO}_2$ , and we believe NGs offer a huge potential to control the co-adsorption of water on the surface of CCMs.

## Experimental Section

Experimental details are given in the Supporting Information.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

carbon capture, carbon dioxide activation, organic–inorganic hybrids, porous materials, surface design

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