DETERMINING THE STRUCTURE OF CHEMISORBED CO_2 SPECIES IN AMINE-FUNCTIONALIZED MESOPOROUS SILICAS BY SOLID-STATE NMR AND COMPUTATIONAL MODELING

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ABSTRACT

Herein we report on detailed spectroscopic and computational study of mesoporous silicate SBA-15 functionalized with primary and secondary amines and loaded with ^{13}C-labeled CO_2[1]. One and two-dimensional solid-state nuclear magnetic resonance (SSNMR) experiments were performed on such samples and revealed unprecedented structural details about the formation of CO_2 adducts from its reaction with various amines. Three chemisorbed CO_2 species were identified by NMR from distinct carbonyl environments resonating at $\delta_C \approx$ 153, 160, and 164 ppm, and their structures were elucidated by additional NMR measurements and computational models.

Keywords: NMR, CO_2, SBA-15, amines.

INTRODUCTION

In the struggle to reduce CO_2 concentrations in the Earth's atmosphere to prevent an increase in the greenhouse effects, the scrubbing of flue gases from stationary sources is assuming a critical role. In recent years, several adsorbent materials have been studied for the selective adsorption/capture of CO_2 in order to substitute the classical scrubbing of gases with aqueous amine solutions. Absorption with these solutions poses several disadvantages, including corrosion problems and the low energy efficiency due to the high temperatures used in the regeneration step. Among the materials that are being developed, amine-functionalized porous sorbents are the most significant ones[2,3] as they have high selectivity and capacity toward CO_2 at low partial pressures even in the presence of moisture[4–6]. This is an advantageous feature for postcombustion gas capture applications where CO_2 exists at relatively low concentrations. Mesoporous silicas, such as SBA-15 used in this work, are widely used to introduce high amounts of covalently tethered amines (typically above 2 mmol g^{-1}, up to 4−5.8 mmol g^{-1})[7,8] since they are very stable and have pores that can facilitate the functionalization process. Although high production cost and difficult scale-up may impair certain future large-scale applications of these materials, the high selectivity and energetic efficiency make them very attractive for special industrial applications like air purification by selective extraction of CO_2[9].

The goal of our study was to detailedly inspect the adsorbate - adsorbent, i.e. CO_2 - amine-functionalized SBA-15, interactions as their understanding is crucial for propelling porous adsorbent design toward ideal CO_2 adsorption-desorption behavior. It is important to obtain a reliable molecular identification of formed species before CO_2 sorption and oxidation-induced degradation studies can be interpreted, since molecular moieties derived from degradation of amines will strongly depend on the chemical nature of CO_2-amine adducts formed in the first place.

EXPERIMENTAL

^{1}H, ^{29}Si, and ^{13}C NMR spectra were acquired on Bruker Avance III 400 and 700 spectrometers operating at B_0 fields of 9.4 and 16.4 T, respectively, with ^{1}H/^{29}Si/^{13}C Larmor frequencies of 400.1/79.5/100.6 MHz and 700.1/139.1/176.1 MHz, respectively. All experiments were performed on either double-resonance 4 mm or 2.5 mm Bruker MAS probes or triple-resonance 4 mm Bruker MAS probe.

RESULTS AND DISCUSSION

To examine the effects of amines with different steric hindrances on CO_2 sorption, we functionalized the mesoporous SBA-15 with primary (APTES) and secondary (TMMAP) amines and thus obtained APTES@SBA-15 and TMMAP@SBA-15 matrices, respectively. Different amines were shown to form distinct hydrogen bond (HB) networks upon CO_2 adsorption, which may explain the different affinity of the materials for CO_2. Adsorption of $^{13}CO_2$ at variable pressures followed by a detailed SSNMR study unveiled the complexity of the system and revealed that several chemisorbed CO_2 species are formed even when just one type of amine is present. Experimental SSNMR combined with quantum mechanical calculations of ^{1}H and ^{13}C chemical shifts (CS) pointed toward the formation of CO_2 adducts stabilized through different combinations of HBs involving neighboring amine molecules and/or silanol groups from the silica surface. This approach allowed for detailed insight into the nature of the intermolecular interactions involved in the formation of CO_2 adducts. To summarize the main results obtained by SSNMR; three ^{13}C resonances, named A, B, and C, resonating between 150 and 170 ppm, are present which indicates the existence of at least three chemisorbed CO_2 species (essentially carbamic acid and alkylammonium carbamate-like ion pairs) in amine-modified SBA-15 materials APTES@SBA-15 and TMMAP@SBA-15 (Fig. 1).

Experimental data for species C, resonating at ^{13}C chemical shift of $\delta_C \approx 164$ ppm, indicate that the OH and the C=O of the carbonyl are engaged in strong HBs with a neighboring amine and a surface OH group, respectively. Both experimental and computational results point to a species C having the carbonyl group strongly bound by HB with a high polarization of the atoms involved in these bonds.

The most deshielded ^{1}H CS was observed at approx. 12 ppm and is only present for alkylamines comprising a secondary amine; the ^{1}H–^{13}C HETCOR NMR spectra of the materials grafted with secondary amines showed that this proton environment is only correlated with ^{13}C resonance B. A ^{1}H CS > 10 ppm suggests that this carbon environment is associated with a species involved in very strong HB with adjacent amines. Calculations demonstrated that this

^{1}H CS was in very good agreement with an HB of the type -RNCOOH···NH$_2$R, while also describing accurately the observed ^{13}C CS of species B ($\delta_C \approx 160$ ppm).

Species A, resonating at $\delta_C \approx 153$ ppm, was found to be extremely water-sensitive and, according to our models, is the only structure containing carbamic acid with its OH group not involved in HBs. More accurately, computational model suggest that species A is engaged in very weak HB interactions only through its C=O oxygen atom.

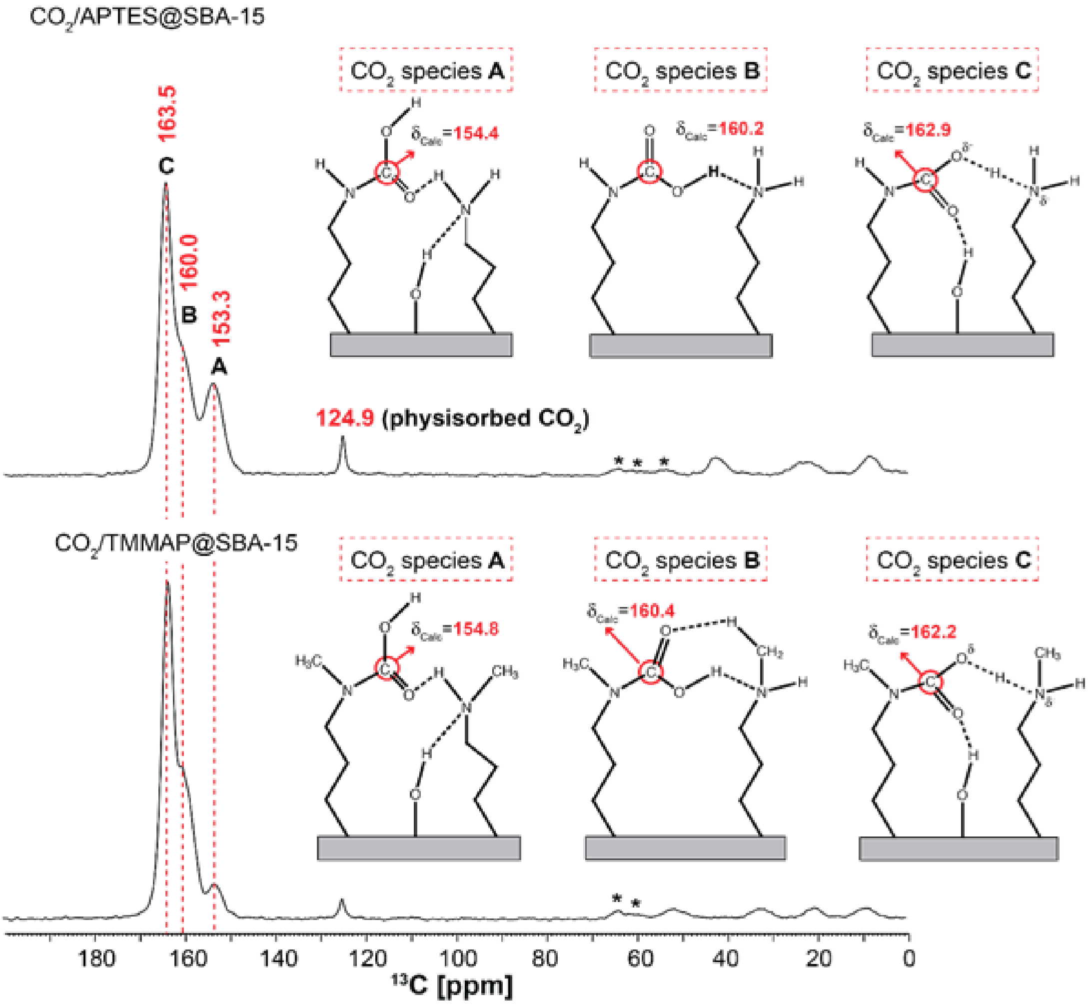

Figure 1. ^{13}C CPMAS NMR spectra of APTES@SBA-15 and TMMAP@SBA-15 loaded with 770 torr of ^{13}CO$_2$ alongside computational models of species A, B and C.

CONCLUSION

The intermolecular interactions involving chemisorbed CO$_2$ species inside amine-modified mesoporous silicas were studied by combination of SSNMR and computer modelling, which proved to be very useful approach for such complex systems. By combining the NMR measurements and computational models, we managed to identify and characterize three main species formed by chemisorption of CO$_2$ onto primary and secondary amines.

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