

# Sorption Mechanism of CO<sub>2</sub> in Amine-functionalized SBA-15 Mesoporous Silica

## Studied by Solid-state NMR Spectroscopy

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### Abstract

Capture of CO<sub>2</sub> via amine-functionalized SBA-15 mesoporous silica has attracted considerable attentions due to its high adsorption capacity and superior durability. However, the detailed mechanism invoked for such gas/solid sorption system remains largely unknown. Herein, we explore the sorption mechanism of CO<sub>2</sub> on an as-synthesized tetraethylenepentamine (TEPA)-modified SBA-15 (sample denoted as P5N-*x*, where *x* is the TEPA loading) by means of various solid-state NMR techniques. Results obtained from <sup>1</sup>H-<sup>29</sup>Si HETCOR NMR experiments revealed that, upon a mild loading of TEPA (ca. 10 wt%) onto SBA-15, resonance peaks responsible for correlations of the hydroxyl groups and the surfactant template (triblock copolymer; P123) with the Q<sup>3</sup> [Si(OSi)<sub>3</sub>OH] and Q<sup>4</sup> [Si(OSi)<sub>4</sub>] surface silica sites of the support were completely replaced by correlations arising from the grafted amines with the surface silica sites. This indicates that the strong hydrogen bonding (C-NH<sub>x</sub>...H-O-Si) between the latter two tends to expel the P123 template from the silica surfaces. That the correlations between the grafted amines with the surface silica sites remain practically unchanged even after adsorption of CO<sub>2</sub> further reveals that while the surface silanols promotes the stability of grafted amines, they were not directly involved during sorption of CO<sub>2</sub>.

**Keywords:** CO<sub>2</sub> capture, amine-functionalization, mesoporous silica, adsorption mechanism, NMR spectroscopy.

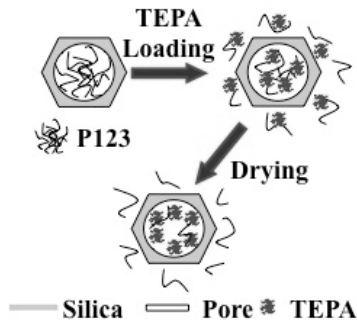
### 1. Introduction

The global awareness of the human impact on the Earth biosphere has increased considerably in recently years, especially the problems of global warming due to the high concentration of green-house gases (GHGs; in particular CO<sub>2</sub> pollutant) in atmosphere. As such, CO<sub>2</sub> capture and sequestration (CCS) has drawn much R&D attentions over the past decade. To confront the issue of CO<sub>2</sub> capture, a wide range of approaches including liquid absorbents [1-4], cryogenic techniques [5], membranes [6,7], and solid adsorbents [8-10], have been proposed and investigated. Although liquid alkanolamines, mostly primary and secondary amines, are effective for CO<sub>2</sub> scrubbing, they are known to suffer from drawbacks such as low uptake capacity, high equipment corrosion rate, high absorbent makeup rate, and high energy consumption during operation etc. As such, solid adsorbents, which are much easier to handle and possess high durability and reusability are more desirable for capture and separation of CO<sub>2</sub>. Among the solid adsorbents, such as microporous zeolites, activated carbons, hydrotalcites, lithium zirconates, calcium oxides, and organic-inorganic hybrids etc. [11], amine-modified mesoporous silicas have been shown to have high adsorption capacity and superior durability for CO<sub>2</sub> capture [12-14]. However, while most investigations concerning CO<sub>2</sub> capture by amine-modified solid adsorbents were mostly focusing on the improvement of uptake performance, spectroscopic investigations at the atomic level are rare. As such, detailed mechanisms

invoked during adsorption and desorption process of such gas/solid sorption system remains largely unknown. Herein, we employ solid-state NMR spectroscopy to investigate the sorption mechanism of CO<sub>2</sub> on as-synthesized tetraethylenepentamine (TEPA)-modified SBA-15 (sample denoted as P5N-*x*, where *x* is the TEPA loading). The role of surfactant P123 on CO<sub>2</sub> absorption is also discussed.

## 2. Experimental Section

**2.1. Sample preparation.** As-synthesized SBA-15 (denoted as as-SBA-15) were prepared according to the literature [15] without removing the surfactant template (P123). Surface functionalization of TEPA was done by introducing ca. 0.2 g of as-SBA-15 with 8 g ethanol in a RB flask, followed by adding desirable amount of TEPA. After stirring at 353 K for 2 h under N<sub>2</sub> atmosphere, the mixture was put into an oven for solvent extraction at 353 K, and the resultant P5N-*x* sample (*x* represents the weight ratio of amine to the total adsorbent).



**Fig. 1.** Schematic of preparation procedure for the TEPA-modified as-SBA-15.

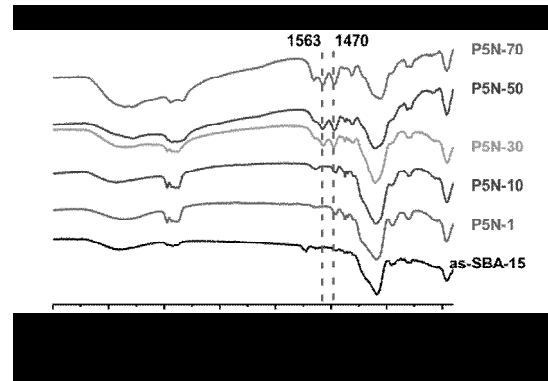
**2.2. Characterizations.** Fourier-transform infrared (FT-IR) spectra were recorded on a Bruker IFS-28 spectrometer at room temperature using KBr pellets. Elemental analyses (EA) were carried out on a CHN elemental analyzer (Heraeus VarioEL-III). The sorption capacities of CO<sub>2</sub> on various solid adsorbents were evaluated by means of a thermogravimetric analyzer (Netzsch TG-209) with 15% dry CO<sub>2</sub> gas flow. All NMR experiments were carried out on an AVANCE-III 500 Bruker-Biospin spectrometer with Larmor frequencies of 126, 51, and 99 MHz for <sup>13</sup>C, <sup>15</sup>N, and <sup>29</sup>Si, respectively, on a 4-mm MAS probehead.

**Table 1:** CO<sub>2</sub> sorption performances of various P5N-*x* under 15% dry CO<sub>2</sub> (gas flow rate of 40 mL/min; 358 K).

Sample	N (wt%) <sup>a</sup>	Amine/sorbent (wt%)	CO <sub>2</sub> uptake (mg/g) <sup>b</sup>	N (mmol/g)	CO <sub>2</sub> /N (mmol/mmol)
P5N-1	0.26	0.71	1.1	0.2	0.15
P5N-10	3.27	8.85	11.4	2.3	0.11
P5N-30	9.93	26.85	72.2	7.1	0.23
P5N-50	15.26	41.28	143.7	10.9	0.30
P5N-60	19.96	53.98	190.5	14.3	0.31
P5N-70	22.88	61.86	226.8	16.3	0.32
P5N-80	26.67	72.12	228.0	19.0	0.27
P5N-85	29.74	80.41	101.9	21.2	0.11
P5N-90	30.26	81.82	90.0	21.6	0.10

<sup>a</sup> Determined by elemental analysis.

<sup>b</sup> Determined by TGA.

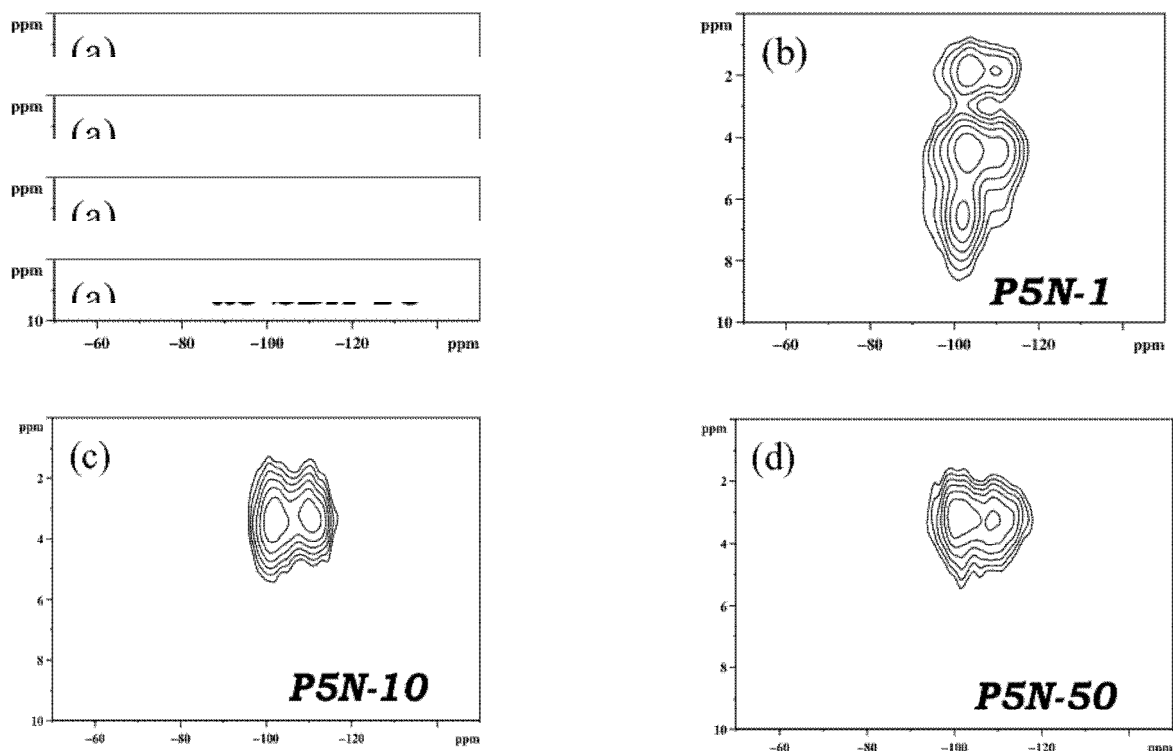


**Fig. 2.** FT-IR spectra of various P5N-*x* samples revealing the presence of primary amines ( $\nu_{N-H}$ ).

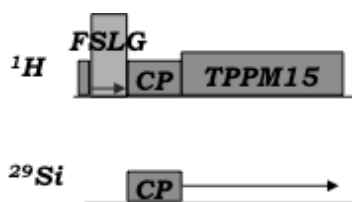
## 3. Results and Discussion

**3.1. Characterization of P5N-*x*** The FT-IR spectra of various TEPA-modified as-SBA-15 (i.e., P5N-*x*) shown in Fig. 2 all exhibit the presence of bending vibration (1563 and 1470 cm<sup>-1</sup>) of the primary amine (RNH<sub>2</sub>) [16]. Together with the fact that the intensities of these bands increase with increasing loading of TEPA, revealing that TEPA was indeed successfully grafted on the surfaces of the as-SBA-15. The amounts of grafted TEPA on each P5N-*x* sample, as evaluated by EA, are depicted in Table 1.

**3.2. CO<sub>2</sub> uptake performance** The CO<sub>2</sub> sorption capacities of the P5N-*x* series samples, as determined gravimetrically by a modified TGA apparatus, are also summarized in Table 1. It is noteworthy that the uptake of



**Fig. 4.** 2D  $^1\text{H}$ - $^{29}\text{Si}$  FS LG-CP HETCOR NMR spectra of (a) as-SBA-15, (b) P5N-1, (c) P5N-10, and (d) P5N-50.



**Fig. 3.** Schematic illustration of the 2D  $^1\text{H}$ - $^{29}\text{Si}$  FS LG-CP HETCOR NMR pulse sequence.

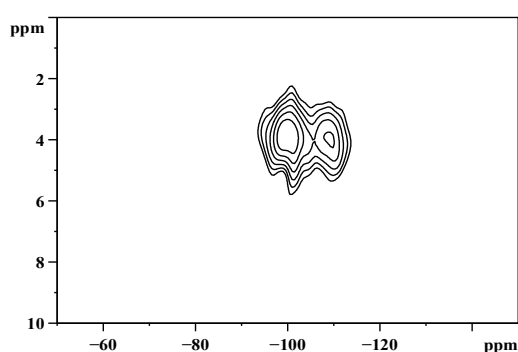
$\text{CO}_2$  observed for the P5N- $x$  solid adsorbents report herein are far superior than the benchmark value (88 mg/g) anticipated for commercialization, except for the sample with extremely low TEPA loading (P5N-1). Among them, P5N- $x$  with TEPA loading ( $x$ ) ca. 70 ~ 80% are found to have the best performance with  $\text{CO}_2$  uptake capacity surpassing 225 mg/g. Moreover, satisfactory performances on rates of adsorption and desorption (ca. 5 and 30 minutes, respectively) were found for samples with optimal uptake capacities (*viz.* P5N-70 and P5N-80). Nonetheless, the highest C/N ratio observed was 0.32 (P5N-70), which is

less than the theoretical value of 0.5. As such, it is hypothesized that ca. 1/3 of the amines were consumed during surface grafting process and hence are inaccessible to the  $\text{CO}_2$  adsorbate during uptake measurements [13,14].

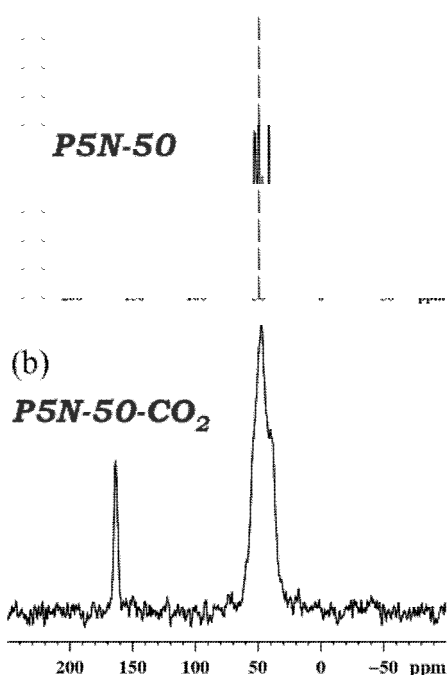
### 3.3. Solid-state NMR characterization of P5N- $x$ adsorbent materials

Two-dimensional (2D)  $^1\text{H}$ - $^{29}\text{Si}$  FS LG-CP HETCOR NMR experiments [17] (Fig. 3) were carried out to probe the correlations between proton and silicon, and the pulse sequences are shown in Fig. 3. As shown in Fig. 4a, the spectrum observed for the as-SBA-15 sample shows more intense  $^1\text{H}$ - $^{29}\text{Si}$  correlation signals provoked mostly by the  $\text{Q}^3$  site with weak signal accounting for  $\text{Q}^4$ . This is in agreement with the notion that  $\text{Q}^3$  species are more abundant than  $\text{Q}^4$  on the pore surfaces of the pristine as-SBA-15. The  $^1\text{H}$  resonance at ca. 6 ppm, which correlates to the  $\text{Q}^3$  sites, may be attributed to hydroxyl protons that are interacting with the oxygen atoms of the surfactant (P123) molecules through hydrogen bonding. Whereas the  $^1\text{H}$  signals at ca. 3.4 ppm may be assigned due to  $-\text{CH}_2-$  of the P123. For P5N-1 (Fig. 4b), an additional  $^1\text{H}$  signal at ca. 1.8 ppm emerges at expense of

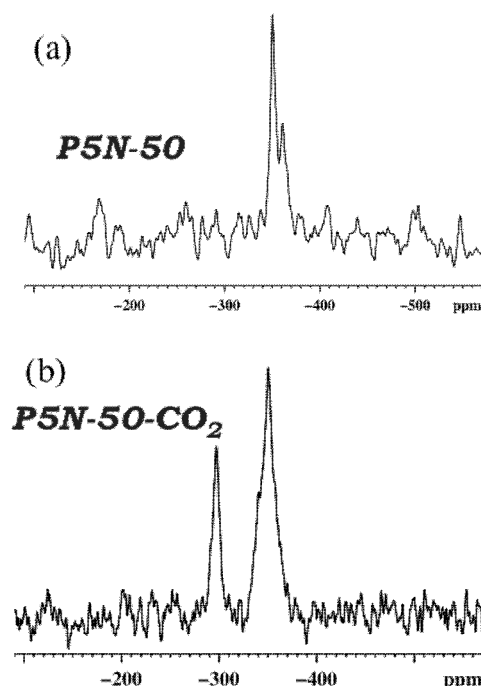
the peak at ca. 6.0 ppm, they can be ascribed due to bare silanol groups on the silica surfaces. Upon increasing TEPA loading (Figs. 4c and 4d), the correlation peak responsible for interactions between surface hydroxyl protons and P123 surfactant diminished, indicating that most P123 molecules were extracted from the surfaces during the functionalization treatment. That the  $^1\text{H}$  signal at 3.4 ppm enhanced upon increasing amine loading indicates that there is a strong affinity between amine and surface hydroxyls on the pore surfaces, at which TEPA are highly dispersed.



**Fig. 5.** 2D  $^1\text{H}$ - $^{29}\text{Si}$  FS LG-CP HETCOR NMR spectrum of P5N-50 in the presence of adsorbed  $\text{CO}_2$ .



**Fig. 6.**  $^{13}\text{C}$  CP-MAS NMR spectra of P5N-50 (a) before, and (b) after  $\text{CO}_2$  uptake.



**Fig. 7.**  $^{15}\text{N}$  CP-MAS NMR spectra of P5N-50 (a) before, and (b) after  $\text{CO}_2$  uptake.

**3.4.  $\text{CO}_2$  adsorption mechanism** Figure 5 shows the  $^1\text{H}$ - $^{29}\text{Si}$  FS LG-CP HETCOR NMR spectrum of the P5N-50- $\text{CO}_2$  sample recorded after adsorbing  $\text{CO}_2$ . That the spectrum is practically the same with that of P5N-50 alone, suggesting that there is no significant interactions between  $\text{CO}_2$  and amine groups at the interfaces. The  $^{13}\text{C}$  CP-MAS NMR spectra observed for P5N-50 before and after  $\text{CO}_2$  uptake are depicted in Fig. 6. The signals in the range between 30 ~ 65 ppm are attributed to methylene groups in TEPA, whereas the peak at 164 ppm (Fig. 6b) may be unambiguously assigned due to the adsorbed  $\text{CO}_2$ . The broadening of the  $^{13}\text{C}$  signals in the 30 ~ 65 ppm region after adsorption of  $\text{CO}_2$  reflects a strong intermolecular interaction between  $\text{CO}_2$  and grafted TEPA. Moreover, no traces of  $^{13}\text{C}$  signal responsible for P123 surfactant were found, indicating that the surfactant molecules are quite mobile and tend to be phase-separated from the surface upon introducing TEPA. The  $^{15}\text{N}$  CP-MAS NMR spectrum of P5N-50 (Fig. 7a) reveals two peaks at -350 and -360 ppm due to the presence of -NH- and - $\text{NH}_2$  groups, respectively. Upon sorption of  $\text{CO}_2$ , the  $^{15}\text{N}$  peak at -360 ppm disappeared while a new peak at ca. -297 was observed (Fig. 7b), which can be attributed to the

presence of carbamate (RNHCOO<sup>-</sup>) species [18-21] formed in the presence of CO<sub>2</sub>.

#### 4. Conclusions

Surface TEPA-functionalized mesoporous as-SBA-15 adsorbent materials with superior CO<sub>2</sub> uptake capacities upto ca. 230 mg/g have been successfully synthesized. Results obtained from <sup>1</sup>H-<sup>29</sup>Si FS LG-CP HETCOR NMR revealed that, upon loading TEPA onto as-SBA-15, surfactant P123 originally retained in the mesoporous channels of the silica substrate tend to be replaced by the grafted amines. This indicates that there is a strong hydrogen bonding (C-NH<sub>x</sub>...H-O-Si) between the grafted amines and the silica pore walls, resulting in extraction of the P123 template from the silica surfaces. Further experiments by solid-state multinuclear NMR revealed that the surface silica sites remain practically unchanged even after adsorption of CO<sub>2</sub>, indicating that while the surface silanols promotes the stability of grafted amines, they were not directly involved during sorption of CO<sub>2</sub>. Furthermore, Upon sorption of CO<sub>2</sub> onto the amine-functionalized silica adsorbents, formation of carbamate species was identified. Additional <sup>13</sup>C/<sup>14</sup>N REAPDOR experiments [22] have been undertaken to directly explore the dipolar couplings between the adsorbed <sup>13</sup>CO<sub>2</sub> and the grafted amines. Such NMR studies are anticipated to render new understanding of detailed sorption mechanism invoked during uptake of CO<sub>2</sub> in amine-functionalized mesoporous silicas and hence should be favorable for future development, design, and implementation of relevant gas/solid systems.

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