

## Supporting Information

# Hybrid Materials for CO<sub>2</sub> Up-take from Simulated Flue-gases: Xerogels Containing Diamines

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### S1. *Experimental details: General procedures*

Unless otherwise specified, all reactions were conducted under dinitrogen using vacuum line systems. Solvents used were dried and stored under dinitrogen. Silyl-alkyl-amines were purchased from Fluka and used as received. CO<sub>2</sub> was purchased from RIVOIRA (99.999 % purity). N<sub>2</sub>/CO<sub>2</sub> mixtures were prepared in our laboratory and the composition determined by GC. Reactions were monitored and analyzed by GC-MS (Shimadzu QP5050, MDN-5S capillary column: 30 m, 0.25 mm, film). FTIR spectra were recorded with a Shimadzu IR Prestige 21 apparatus. Nuclear Magnetic Resonance-NMR experiments were carried out with a 400 MHz Varian INOVA apparatus. Chemical shifts ( $\delta$ , ppm) were determined relative to the solvent and converted to the  $\delta$  scale downfield from Me<sub>4</sub>Si. The absorption/desorption of carbon dioxide was monitored by GC-TCD using a DANI gaschromatograph.

### S2. *Procedures for the uptake of CO<sub>2</sub>*

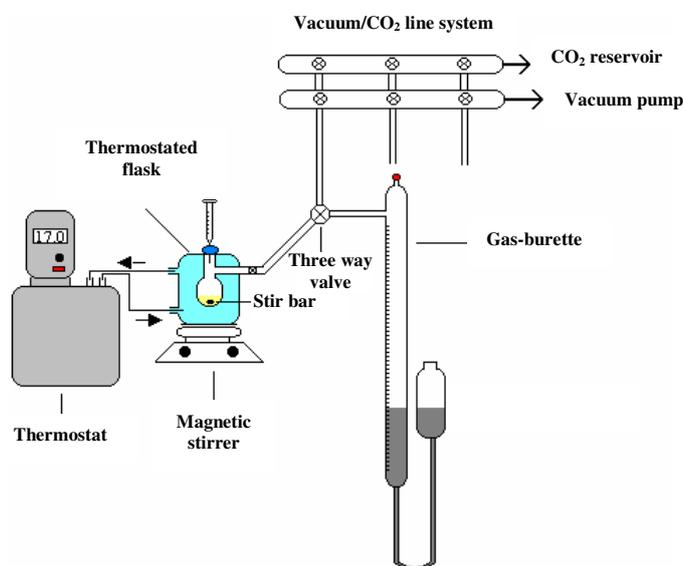
CO<sub>2</sub> uptake was monitored using a round bottomed thermostated flask (15 mL) (See Scheme 1) connected to a gas-burette that allowed to measure the uptaken (low temperature) or released (high temperature) CO<sub>2</sub>. The temperature of the thermostatic liquid was set according to the operation. The flask was closed with a rubber septum to make easier the addition of the amine. A water bath

was used to heat the flask at  $297\pm 1$  K, an oil bath allowed to bring the temperature up to 410 K, while a cryostat was used to carry the reaction at  $273\pm 1$  K (Scheme 1).

### S2.1 General procedure for measuring the amount of $\text{CO}_2$ up-taken by the amine.

5 mL of THF was introduced into the thermostated flask under  $\text{CO}_2$  atmosphere and saturated with  $\text{CO}_2$  ( $P_{\text{CO}_2} = 0.1$  MPa). Then, through the rubber septum, amine **1** (0.18 mL, 1.02 mmol) or **2** (0.15 mL, 0.64 mmol) or **3** (0.15 mL, 0.68 mmol) or MEA (0.25 mL, 3.69 mmol) was added. The absorption of  $\text{CO}_2$  was monitored during the time keeping constant the pressure of the gas by rising the reservoir of mercury. Knowing the temperature (thermostatic liquid), the volume (measured with the burette. It is opportune to specify that the volumes of tubing and connections are less than 1% of the volume of the flask) and the pressure (ambient atmospheric pressure measured apart, close to 0.1 MPa) it was possible to calculate the mmol of  $\text{CO}_2$  up-taken by the known amount of the amine. The data are reported in Figures 1 and 2.

When the release of  $\text{CO}_2$  was studied, the temperature was increased pumping a hot fluid through the double walled cell and the amount of released  $\text{CO}_2$  was calculated by measuring its volume at the given pressure (close to 0.1 MPa, as in the up-take) and temperature. In this case the reservoir of mercury was lowered with respect to the initial position to keep constant the pressure.



**Scheme 1.** Apparatus used for the  $\text{CO}_2$  up-take/release.

When xerogels were used, the xerogel was deposited on the wall of the cell (the mass was determined by double weighting) and the uptake/release of  $\text{CO}_2$  was followed in the same way as above. The amount of amine per unit-mass xerogel was determined by N-analysis on the solid sample.

## S2.2 Isolation of ammonium carbamates

When amines **1-3** in THF were contacted with CO<sub>2</sub> at 0.1 MPa, a white solid was formed that was isolated by filtration in an inert atmosphere, washed with pentane (2x5 mL) and dried in a CO<sub>2</sub> flow at 300 K. The carbamates formed during the reaction of amines **1-3** with CO<sub>2</sub> were characterized by <sup>1</sup>H, <sup>13</sup>C NMR (see Table 1) and elemental analyses.

Anal. Calc. for C<sub>13</sub>H<sub>34</sub>N<sub>2</sub>O<sub>8</sub>Si<sub>2</sub> (from amine **1**):

C = 38.78, H = 8.51, N = 6.95 %; Found C = 38.68, H = 8.45, N = 6.90 %.

Anal. Calc. for C<sub>19</sub>H<sub>46</sub>N<sub>2</sub>O<sub>8</sub>Si<sub>2</sub> (from amine **2**):

C = 44.33, H = 9.00, N = 5.44 %; Found C = 44.12, H = 9.18, N = 5.68 %.

Anal. Calc. For C<sub>9</sub>H<sub>22</sub>N<sub>2</sub>O<sub>5</sub>Si (from amine **3**):

C = 43.14, H = 7.96, N = 10.05 %; Found C = 43.25, H = 8.08, N = 10.18 %.

## S3. Procedures for the preparation of xerogel and its use as sorbent of carbon dioxide

Amine **3** (0.5 mL, 2.29 mmol) was mixed, under dinitrogen, with methanol (0.5 mL, 12.37 mmol). To this solution 0.1 mL of HCl (0.1 M in CH<sub>3</sub>OH) were added with Si(OCH<sub>3</sub>)<sub>4</sub> (0.5 mL, 3.73 mmol). Very rapidly a gel suspension was formed which was dried under *vacuum* at max 300 K to obtain a white powder that remained adherent to the walls of the flask. The xerogel was analyzed by FTIR. Two bands at 1147 e 1048 cm<sup>-1</sup> due to stretching of Si-O-Si bond were observed. Broad bands due to NH bonds were present in the spectrum. Aliphatic C-H bonds were evident at 2800-3000 cm<sup>-1</sup>. The xerogel remained as a film adherent to the walls of the flask. An attempt to measure the BET gave very variable values ranging from 5 to 110 m<sup>2</sup>/g, depending on the preparation (rate of drying) and isolation conditions. The rate of uptake of CO<sub>2</sub> was sensitive to BET. In the uptake/release experiments described here, a material with a BET equal to 40 m<sup>2</sup>/g was used.

The xerogel was then used as sorbent of CO<sub>2</sub> (Figure 5 in the text). In a typical experiment, the xerogel was formed adherent to the bottom of the measurement cell as a thin film. After drying as reported above, the cell was connected to the equipment shown in Scheme 1 and the uptake/release of CO<sub>2</sub> followed as described above (S2.1).

In a similar way xerogels of amine **1** and **2** were prepared. Their ability to uptake CO<sub>2</sub> was less than 2% than amine **3**.

#### S4. Procedures for the preparation of carbamic acids of amines 1 and 2

A thin film of amine **1** or **2** was contacted with CO<sub>2</sub> at 273 K. A glassy material was formed after 1 h that was analysed by <sup>13</sup>C NMR to show the presence of the carbamic moiety different from that of the carbamate (Table 1).

Table 1. <sup>1</sup> H and <sup>13</sup> C NMR spectra for carbamates and carbamic acids of amines <b>1-3</b>							
	<sup>1</sup> H NMR						
Compound	NH <sub>2</sub>	CH <sub>2</sub> α	CH <sub>2</sub> β	CH <sub>2</sub> γ	CH <sub>2</sub> δ	CH <sub>2</sub> ε	OR
1	1.78	2.64	1.64	0.68			3.54 (CH <sub>3</sub> )
2	1.27	2.68	1.56	0.64			3.82 (CH <sub>2</sub> ) 1.24 (CH <sub>3</sub> )
2'		2.72(α) 3.05(α')	[a]	[a]			[a]
3	1.75	2.75	2.57	2.57	1.57	0.63	3.52 (CH <sub>3</sub> )
3'	3.52	vb <sup>[b]</sup>	3.05	2.15	1.7	0.65	3.57 (CH <sub>3</sub> )
	<sup>13</sup> C NMR						
Compound	N-C(O)O-	CH <sub>2</sub> α	CH <sub>2</sub> β	CH <sub>2</sub> γ	CH <sub>2</sub> δ	CH <sub>2</sub> ε	OR
1		44.8	26.7	6			50.4 (CH <sub>3</sub> )
1'	163						
1''	158.3						
2		45.2	27.3	7.7			58.40 (CH <sub>2</sub> ) 18.36 (CH <sub>3</sub> )
2'	163.1						
2''	158.2						
3		41.6	52.2	52.2	23.3	6.7	50.2 (CH <sub>3</sub> )
3'	163	vw <sup>[c]</sup>	38.2	38	20	5.8	50.5 (CH <sub>3</sub> )
[a] unchanged with respect to the starting amine; [b] very broad; [c] very weak. See Fig. 1 for the labelling of C-atoms of mono-amines, Fig. 2 for the labelling of di-amines, Fig. 3 for the labelling of compound 3'.							