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# CO<sub>2</sub> capture and CO<sub>2</sub>/CH<sub>4</sub> separation by silicas with controlled porosity and functionality

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## Abstract

Microporous, mesoporous and hydrophobic silica materials with high specific surface area are obtained by an easy and cheap sol-gel synthesis. The effect of pore size and of water content on gas adsorption and separation are investigated. We also identified the relative amounts of different types of water in the porous silica, around 25% and 75% for bound and free water. The kinetics of rehydration is extremely slow, 60 % recovery after 4 days implying that the material can be used as is over several hours. Adsorption isotherms of pure gaseous CO<sub>2</sub> and CH<sub>4</sub>, and of their mixtures at different pressures, show that among the materials synthesized, the microporous hydrophilic silica exhibits the best performance in terms of CO<sub>2</sub> adsorption capacity (2.8 mmol.g<sup>-1</sup>) and a separation factor over 10 at low CO<sub>2</sub> content and low pressure. Both properties are highly sensitive to the presence of residual water and to terminal chemical groups. This work highlights the possibility to develop competitive and cheap silica materials that could be scaled up to industrial uses.

### Keywords:

CO<sub>2</sub> capture, CO<sub>2</sub>/CH<sub>4</sub> separation, storage, porous silica, water, sol-gel synthesis, CCS

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## Introduction

CO<sub>2</sub> emissions from human activities [1] are recognised as the main contribution to the constant increase of atmospheric carbon dioxide (CO<sub>2</sub>) responsible for global warming [2, 3]. CO<sub>2</sub> capture and storage technologies (CCS) are widely explored to mitigate the increasing concentration of CO<sub>2</sub>. Adsorption processes are among the most promising techniques for separating CO<sub>2</sub> from exhaust gases [4]. Finding suitable adsorbents with a large storage capacity and selectivity for CO<sub>2</sub> nonetheless remains challenging.

Much work focused on the capture of atmospheric CO<sub>2</sub>, for which CO<sub>2</sub>/N<sub>2</sub> adsorption efficiency and selectivity are crucial. Carbon-based materials were developed with an optimal content of mono- or multi-hetero atoms like N, S, O in order to maximize the CO<sub>2</sub> adsorption capacity[5, 6]. These materials, combining nitrogen hetero-atoms and microporosity mainly below 0.73 nm achieved CO<sub>2</sub> adsorption over 6.4 mmol.g<sup>-1</sup>. Other studies have focused on both CO<sub>2</sub> adsorption and CO<sub>2</sub>/N<sub>2</sub> selectivity[7, 8, 9], finding that multi-hetero atoms improve CO<sub>2</sub> adsorption as well as CO<sub>2</sub>/N<sub>2</sub> selectivity. In these hetero-atom basic Lewis sites induce affinity for CO<sub>2</sub> while narrow pores discriminate the smaller kinetic radius of CO<sub>2</sub> relative to N<sub>2</sub>.

Separation of CO<sub>2</sub> from CH<sub>4</sub> is also important, *e.g.* in many industrial processes such as natural gas sweetening (*e.g.* CO<sub>2</sub> removal from high pressure methane in natural gas wells), biogas upgrading [10], oil recovery enhancement and landfill gas purification [11]. Developing cheap, efficient techniques for removal and capture of CO<sub>2</sub> in CH<sub>4</sub>, over a wide range of CO<sub>2</sub> concentrations and flow rates is thus important. One promising way to achieve this goal is the use of porous materials [12, 13], *e.g.* Many of them are considered as potential candidates for CO<sub>2</sub> capture as for example, zeolites (5A and 13X) [14], activated carbon [15, 16], mesoporous silica (SBA-15, MCM-41, ...) [17, 18, 19], silica gel [20] and metal organic frameworks[21, 22]. Earlier work showed that CO<sub>2</sub> adsorption performance stems from the combined effects of microporosity and functionalization, again mainly with basic nitrogen functions[23, 24]. Moreover, it is well-known that nitrogen functions efficiently capture CO<sub>2</sub> *via* a chemisorption phenomenon leading to high costs for the regeneration of the materials [25, 26]. We prefer to design an efficient porous silica material favouring physisorption in order to facilitate its regeneration.

Here we report on synthesis and characterisation of silica adsorbants for CO<sub>2</sub>/CH<sub>4</sub> separation, rationalising and optimising the main parameters in-

fluencing the CO<sub>2</sub> adsorption efficiency from gaseous mixtures. We do not use nitrogen functions in order to preserve easy, cheap regeneration of the materials, based on CO<sub>2</sub> physisorption. In particular, we examine the effects of micro- *vs.* mesoporosity, by changing the synthesis pH, and the kinds and amounts of water- free or bound to silica, by modifying the hydrophilicity or hydrophobicity *via* partial methylation. Understanding the role of water is important since it will be present under practical conditions such as temperature under which separation of CO<sub>2</sub> and CH<sub>4</sub> is to be achieved.

## 1. Materials and Methods

### *Synthesis*

Materials are synthesized by sol-gel route from the precursor tetramethoxyorthosilicate (TMOS). Molar ratios are 1/5/4 for alkoxide, methanol and water. The general synthesis protocol used by our group, originally for a completely different application, is described by C. Cantau *et al.* [27]. Two synthesis strategies are developed here: *(i)* modifying the pH to control the porosities; *(ii)* use of a second precursor, trimethoxymethylsilane (TMMS), to induce a degree of hydrophobicity, as summarized in Table 1. Xerogels are dried 10 days at 60°C, 10 days at 30°C, 6 hours at 60°C and finally 2 days at 80°C.

Material	$S_{\text{ref}}$	$S_{\text{pH9}}$	$S_{\text{TMMS}}$
Precursor	TMOS	TMOS	60% TMOS + 40% TMMS
Synthesis pH	6	9	6
Characteristics	Microporous hydroxylated	Mesoporous hydroxylated	Microporous partially methylated
Physisorbed water (wt%)	11	8	5
Hydroxyl groups (wt%)	5	4.5	9 <sup>a</sup>
Organic matter (wt%)	2	1	
Specific surface area(m <sup>2</sup> .g <sup>-1</sup> )	700	580	85/250 <sup>b</sup>
Free water fraction (%)	75	76	73
Bound water fraction (%)	27	24	27
Ratio	2.7	3.2	2.7

Table 1: **Synthesis conditions and properties of the present materials.**

*b.* Second value refers to CO<sub>2</sub> adsorption.

*a.* sum of hydroxyls and organic matter.

### Characterisation

Several experimental techniques are applied to characterize the materials, particularly adsorbed water, see the SI for details. Diffuse reflectance infra-red Fourier transform (DRIFT) is used to track the influence of heat treatment *via* I.R. band intensities relative to the  $1100\text{ cm}^{-1}$  band of the silica matrix. We probed material texture *via*  $\text{N}_2$  adsorption isotherms and thermogravimetric analysis (TGA). We probe different types of adsorbed water, *e.g.* during rehydration of  $S_{\text{ref}}$ , by near infra-red spectroscopy (NIR), decomposing spectra in the  $4700\text{--}5500\text{ cm}^{-1}$  range into a sum of gaussian contributions. Adsorption of pure and mixed gases is quantified by recording gravimetric or barostatic adsorption isotherms.

## 2. Results and discussion

### *Diffuse Reflectance Infrared Fourier Transform Spectroscopy*

Fig. 1 shows the DRIFT spectra of the three kinds of silica. The dominant  $1100\text{ cm}^{-1}$  band and broad shoulder at  $1170\text{ cm}^{-1}$  ( $\nu_{\text{anti}}(\text{Si-O-Si})$  asymmetric stretch) attest formation of the Si-O-Si framework in all the materials, while the band at  $940\text{ cm}^{-1}$  is due to Si-OH groups ( $\nu(\text{Si-OH})$  stretch)[28, 29]. The  $800\text{ cm}^{-1}$  band is variously attributed in the literature to the  $\delta(\text{Si-OH})$  deformation[28] or to the symmetrical  $\nu_s(\text{Si-O-Si})$  stretch[29, 30]. Here, we find the band is unchanged in heated samples, indicating that it is due to  $\nu_s(\text{Si-O-Si})$  stretching. The hydroxyl stretching band is due to incomplete condensation during synthesis, while the weak but significant bands around  $1400\text{ cm}^{-1}$  and  $2900\text{ cm}^{-1}$ , attributed in refs. [29, 31] to  $\delta(-\text{CH}_3)$  deformation and  $\nu(-\text{CH}_3)$  elongation of methyl groups linked to a silicon atom, imply incomplete hydrolysis. The overall formula of the materials is thus  $(\text{SiO}_{2-y-z})_x(\text{OH})_y(\text{OCH}_3)_z$  with  $y$  and  $z$  small compared to  $x$ . The spectrum of the  $S_{\text{pH9}}$  material (black curve) differs only by the intensity of the bands relative to the reference material  $S_{\text{ref}}$ .

Compared to the reference spectrum (blue), the spectrum of material prepared with 40% of the methylated precursor shows additional bands (red curve): an antisymmetric Si-CH<sub>3</sub> stretching mode at  $2960\text{ cm}^{-1}$ , Si-CH<sub>3</sub> stretching at  $2870\text{ cm}^{-1}$ , antisymmetric -CH<sub>3</sub> deformation at  $1450\text{ cm}^{-1}$ , and -CH<sub>3</sub> symmetric deformation at  $1370\text{ cm}^{-1}$ [31]. The spectrum indicates a silica network with both surface hydroxyl and terminal CH<sub>3</sub> groups.

Water and surface hydroxyl groups in the materials appear in the range  $3000\text{--}3800\text{ cm}^{-1}$ . Thus the broad water stretch band, peaking at  $3300\text{ cm}^{-1}$ ,

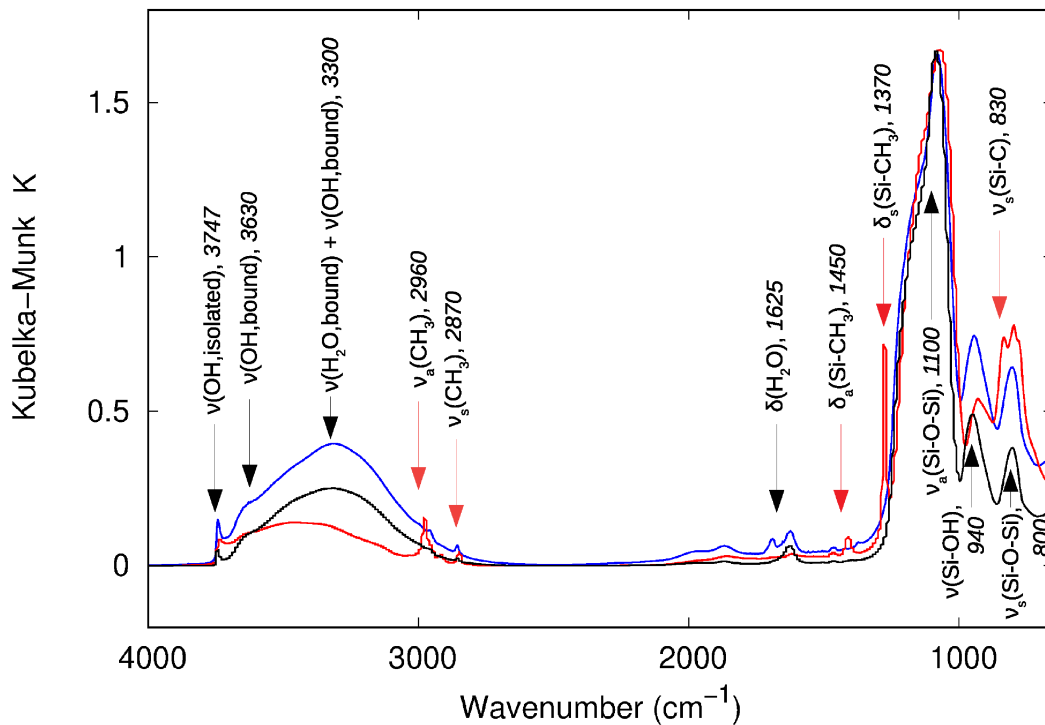


Figure 1: **Main IR bands of the as synthesized materials.** DRIFT spectra of:  $S_{\text{ref}}$  (blue),  $S_{\text{pH9}}$  (black) and  $S_{\text{TMMS}}$  (red), with assignments and positions in  $\text{cm}^{-1}$ . Spectra are normalized on the silica network band at  $1100 \text{ cm}^{-1}$ .

decreases on heating the materials and disappears beyond 400°C, see *e.g.* supplementary Fig. 3. The shoulder at 3630 cm<sup>-1</sup> is due to stretching of hydroxyl groups engaged in hydrogen bonds with water or between vicinal surface silanols[32, 30]. The sharply peaked free hydroxyl stretching band at 3747 cm<sup>-1</sup> indicates isolated or geminal silanols without any interaction with water[32, 30]. Here, it indeed becomes relatively more prominent on heating, as more and more water or hydroxyls are desorbed. Conversely the characteristic bending mode of water[32, 30] around 1625 cm<sup>-1</sup> disappears on heating the sample, supplementary Fig. 3.

#### *Thermogravimetric analysis (TGA)*

TGA, see Fig. 2, quantifies physisorbed water, the density of surface hydroxyls and organic residues such as those left by incomplete hydrolysis. The first, sharp drop, 11% for the reference sample at 150°C corresponds to loss of physisorbed water. It is followed by a slower drop up to 400°C, as surface silanols are driven off, 5% for  $S_{\text{ref}}$  after accounting for 2% loss of organic matter at 400°C. Dehydroxylation is still incomplete at 800°C, making the water contents in table 1 lower bounds. Considering the high organic content of the methylated silica, we report only a net weight loss beyond 150°C.

#### *N<sub>2</sub> isotherms for textural characteristics*

Table 1 reports the porosity data deduced from the N<sub>2</sub> adsorption isotherms shown in Fig. 3. As an indication, the specific surface area of  $S_{\text{ref}}$  varied between 600 and 800 m<sup>2</sup>.g<sup>-1</sup> between synthesis batches. The isotherm of this material is type I(b), with some of the character of type IV, indicating firstly a wide distribution of pore sizes, including micropores and possibly narrow mesopores, and secondly the presence of a small amount of mesopores. A quite different, type IV isotherm with clear hysteresis indicates a majority of mesopores in  $S_{\text{pH9}}$ . However, the similarity of the  $S_{\text{pH9}}$  and  $S_{\text{ref}}$  isotherms at low very pressure implies comparable microporosities, consistent with the lower specific area of  $S_{\text{pH9}}$  compared to  $S_{\text{ref}}$  (table 1). The surprisingly low specific surface area of  $S_{\text{TMMS}}$  would suggest a non-porous material, but the area deduced from CO<sub>2</sub> adsorption (*cf.* inset of Fig. 3) is nonetheless 225 m<sup>2</sup>.g<sup>-1</sup>. The smaller kinetic diameter of CO<sub>2</sub>, compared to that of N<sub>2</sub> [8, 9], may explain this result, then implying the presence of ultra-micropores (*cf.* [8, 9]).



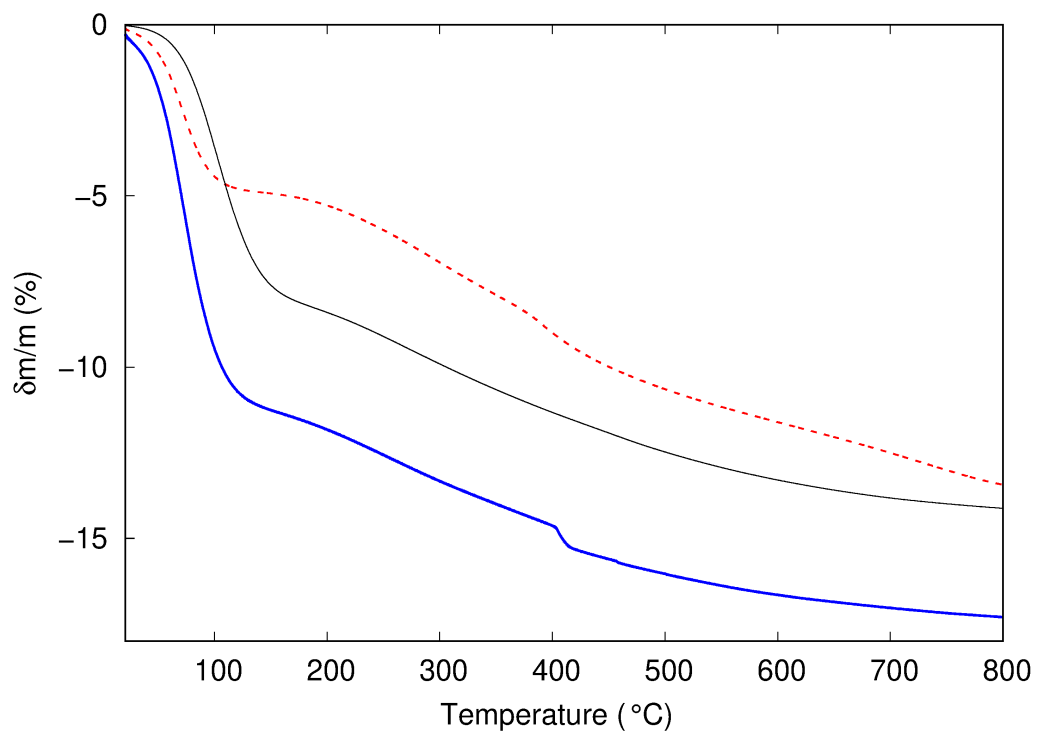


Figure 2: **Loss of water, hydroxyls and organic matter.** Thermogram of  $S_{\text{ref}}$  (blue thick line),  $S_{\text{pH9}}$  (black thin line) and  $S_{\text{TMMS}}$  (red dotted line).

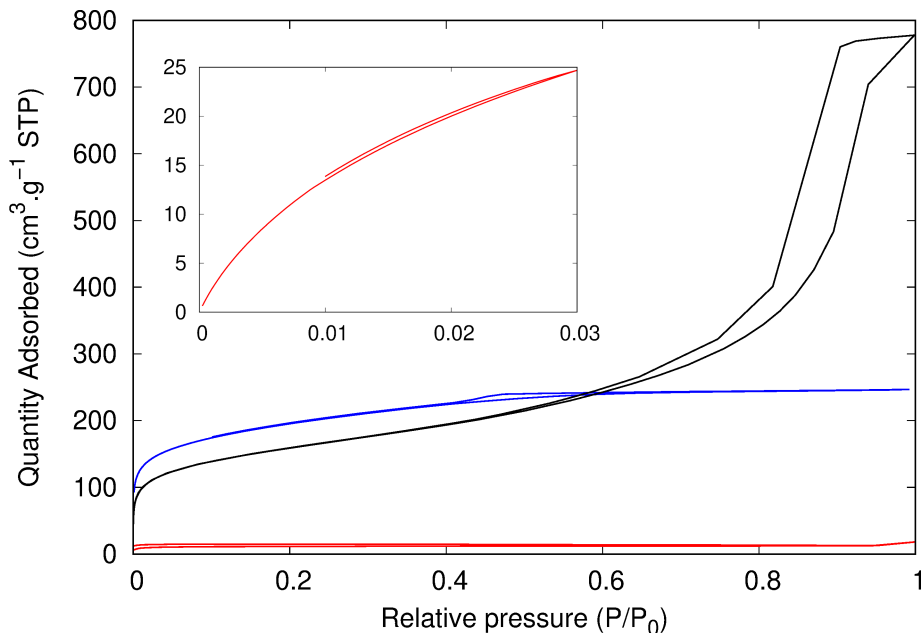


Figure 3:  $N_2$  isotherms of  $S_{\text{ref}}$  (blue),  $S_{\text{pH9}}$  (black) and  $S_{\text{TMMS}}$  (red). inset: adsorption and desorption of  $CO_2$  for  $S_{\text{TMMS}}$  only.

### *Surface density of hydroxyls*

Except for  $S_{\text{TMMS}}$ , where the organic matter strongly screens the surface, we determine the total number of hydroxyl groups from the mass of water lost  $\Delta m$  during the second stage of TGA and the relation[30]:

$$N_{\text{OH}} = \frac{2\Delta m \times N_{\text{A}}}{M_w} \quad , \quad (1)$$

where  $M_w$  is the molecular weight of water,  $N_{\text{A}}$  is Avogadro's number and the factor 2 accounts for the formation of one water molecule per 2 silanols. Combining values with the specific surface areas, we find the density of surface hydroxyls,  $\sigma_{\text{OH}} = 4.8$  and  $5.2 \text{ nm}^{-2}$  for  $S_{\text{ref}}$  and  $S_{\text{pH9}}$ . Considering the estimated 15% uncertainty in the specific surface areas, the materials are equally hydrophilic and are also representative amorphous silicas, for which the average silanol density is  $4.6 \text{ nm}^{-2}$ [33]. Obviously, some inhomogeneity of the distribution of adsorbed water is to be expected. Thus, although the  $\times 2$  ratio between the first and second weight losses under TGA is consistent with a complete surface monolayer of water, with one donating and one

receiving hydrogen bond on every silanol, confirming or contradicting this simple picture requires other information, provided by NIR spectroscopy.

#### *Near-infrared spectroscopy (NIR)*

Relative intensities of the water band  $\approx 3500 \text{ cm}^{-1}$  in the DRIFT spectra of Fig. 1 are consistent with the corresponding specific surface areas, but this band contains contributions from silanols and does help distinguish bound from bulk water. We therefore recorded NIR spectra, basing our interpretation of physisorbed water on the assignment of hydroxyl stretching and water bending combination bands around  $5200 \text{ cm}^{-1}$  in ref. [34], *e.g.* (i) a band at  $5270 \text{ cm}^{-1}$  due to water on (geminal) silanols; (ii) a band at  $5180 \text{ cm}^{-1}$  in bulk water, assigned to combination of  $\nu_2$  ( $1644 \text{ cm}^{-1}$ ) and  $\nu_3$  ( $3490 \text{ cm}^{-1}$ ).

Comparison of the spectra of  $S_{\text{ref}}$  before drying under vacuum at  $120^\circ\text{C}$ , and during rehydration, assists assignment in Fig. 4a. The as synthesised sample shows an asymmetrical peak at  $5200 \text{ cm}^{-1}$ , with a clear shoulder on the lower energy side, and a broad double peak around  $7000 \text{ cm}^{-1}$  (blue curve). On drying (black curve), the  $\approx 5200 \text{ cm}^{-1}$  band in agreement with ref. [34] resolves into a main peak at  $\approx 5250 \text{ cm}^{-1}$  and a low energy shoulder around  $5150 \text{ cm}^{-1}$ . The massif at  $7000 \text{ cm}^{-1}$  transforms into a peak at  $7317 \text{ cm}^{-1}$  and two low energy shoulders. In agreement with ref. [34], we interpret the sharp peak at  $7317 \text{ cm}^{-1}$  as silanols freed by drying, the first shoulder ( $7121 \text{ cm}^{-1}$ ) as water coordinated silanols and the second ( $6861 \text{ cm}^{-1}$ ) as bulk water. Consistent with this, the intensities of the shoulders relative to the sharp peaks recover during rehydration. Recovery is slow, *e.g.* the last spectrum was recorded 4 days after dessication.

Deconvolution of the  $\approx 5200$  band in all the as synthesised samples then provides the proportions of bound and bulk water before drying, see table 1, and the SI for details. Note that although the total amount of water depends on the synthesis, the proportions of free (or bulk) and bound water are the same in all the samples,  $\approx 3 : 1$ , suggesting that water in  $S_{\text{TMMS}}$  is confined to un-functionalised areas of the porous network. Using the specific surface areas, and first and second weight losses in TGA above, we deduce that on average, 1 in 4 silanols in  $S_{\text{ref}}$  hosts a water molecule, and 1 in 5 in  $S_{\text{pH9}}$ .

Employing the same spectral decomposition, we can follow rehydration of dried silica exposed to ambient air. Fig. 4b shows the initial 0-order recovery kinetics of free and bound water in dessicated  $S_{\text{ref}}$ . After 4 days, the recovery of bound water has clearly slowed down (characteristic time 2.5 days in the dashed-line fit to an exponential saturation model, see the SI), whereas the

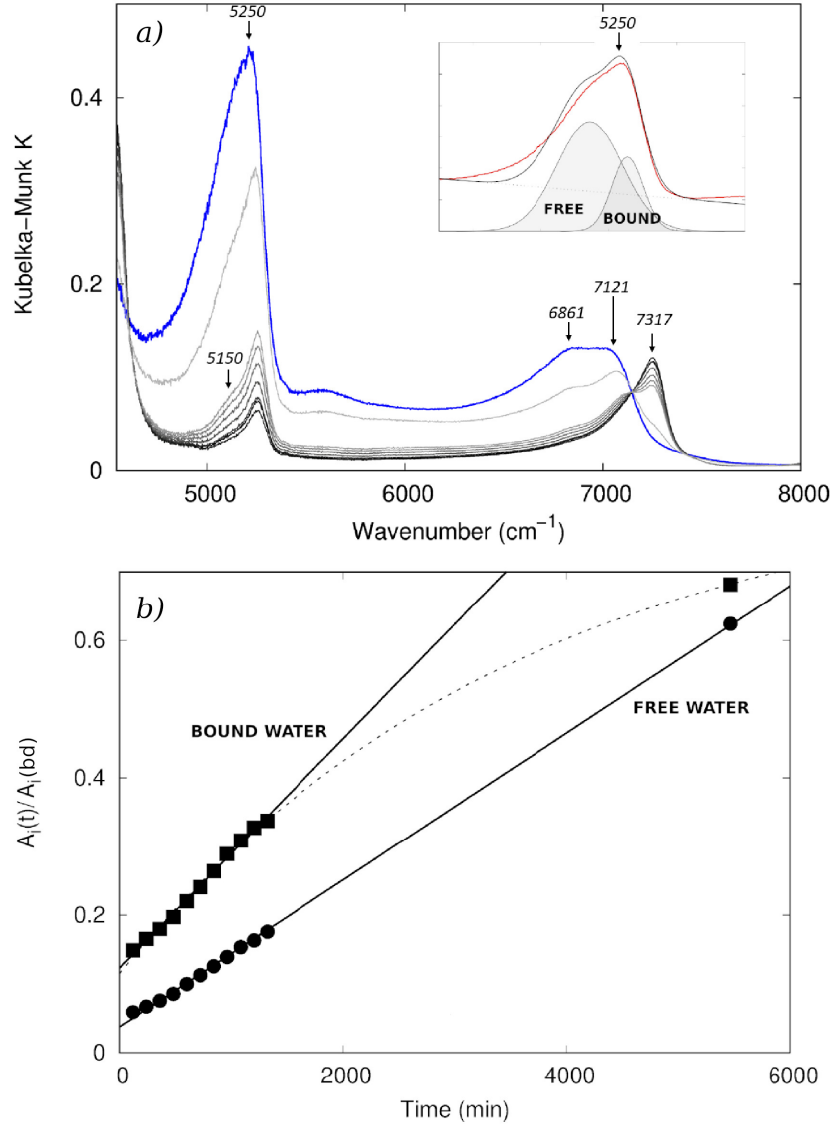


Figure 4: **NIR monitoring of rehydration (ambient conditions) of  $S_{\text{ref}}$  silica, vacuum-dried at  $120^\circ\text{C}$ , assists identification of the physisorbed and bulk water in ambient conditions.** (a) Spectra are shown as synthesised before desiccation (blue) and during rehydration (black to light grey). Inset: example of deconvolution of the experimental spectra into two gaussian contributions. (b) Recovery of bound and free water under ambient conditions, from the deconvolution (See SI).  $A_i(t)$   $i$ =bound or free, is the area of component  $i$  at time  $t$  and  $A_i(bd)$  is the corresponding area before drying. Straight lines show initial zero-order kinetics (rate constants  $k_{\text{bound}} \approx 1.7 \times 10^{-4} \text{ min}^{-1}$  and  $1.1 \times 10^{-4} \text{ min}^{-1}$  ; dashed line: exponential fit to the tailing off of recovery of bound water (see the SI), with characteristic time  $\tau_R = 60 \text{ h}$ .

contribution of free water continues to recover at its initial rate. One possible explanation would be congestion due to already adsorbed water in narrow pores, *cf.* the type I(b) isotherm in Fig. 3.

The above results, show that desiccated  $S_{\text{ref}}$  is not fully dehydrated under the conditions described, and small amounts of residual water may influence gas adsorption. The slowness of rehydration may prove an advantage in applications since it makes drying the gaseous mixture to be separated less important.

### *Gas adsorption*

CO<sub>2</sub> adsorption by  $S_{\text{ref}}$  is improved by pre-baking the as synthesised material under vacuum, see supplementary Fig. 1 and discussion in the SI. The adsorption capacity increases with the baking temperature, but only marginally above 80 °C. Because we find below that leaving some adsorbed water is actually favourable to CO<sub>2</sub> adsorption, and because baking at higher temperatures may drive off some silanols[33], we pre-baked all samples at 80 °C.

Fig. 5 shows the adsorption isotherms of pure CO<sub>2</sub> or CH<sub>4</sub>. The mesoporous silica  $S_{\text{pH9}}$  has the highest capacity for either pure gas. All the silicas adsorb more CO<sub>2</sub> than CH<sub>4</sub> as measured by the ratio of the amounts absorbed from each gas taken separately,  $R = n_{\text{CO}_2}^a/n_{\text{CH}_4}^a$  (commonly called the selectivity for gas mixtures), *cf.* Table 2. As well known, and expected here, microporosity favours CO<sub>2</sub> adsorption relative to CH<sub>4</sub>. Thus, although  $S_{\text{pH9}}$  has the highest capacity for either gas,  $S_{\text{ref}}$  has the best selectivity over the present range of pressures. Ultra-microporosity is known [5, 6] to enhance the adsorption capacity of CO<sub>2</sub>, but here the lower adsorption capacity of  $S_{\text{TMMS}}$  probably is due to its lower specific surface area.

Less expectedly, table 2 also shows that  $S_{\text{TMMS}}$  does not perform as well as  $S_{\text{ref}}$ . The initial assumption was that partial methylation would improve CO<sub>2</sub> adsorption capacity by reducing competition with adsorption of water. But, partial methylation, leads to stronger competition with CH<sub>4</sub> adsorption, and in fact lower selectivity than determined for  $S_{\text{ref}}$ . Moreover, the low specific surface area found for  $S_{\text{TMMS}}$  induces a lower adsorption capacity for both gases. Thus, partial methylation is not the best way to improve both the adsorption capacity and the selectivity.

Silica  $S_{\text{ref}}$  has nearly the same capacity as  $S_{\text{pH9}}$ , but is more selective. Therefore, we measured adsorption isotherms of CO<sub>2</sub>/CH<sub>4</sub> mixtures only on

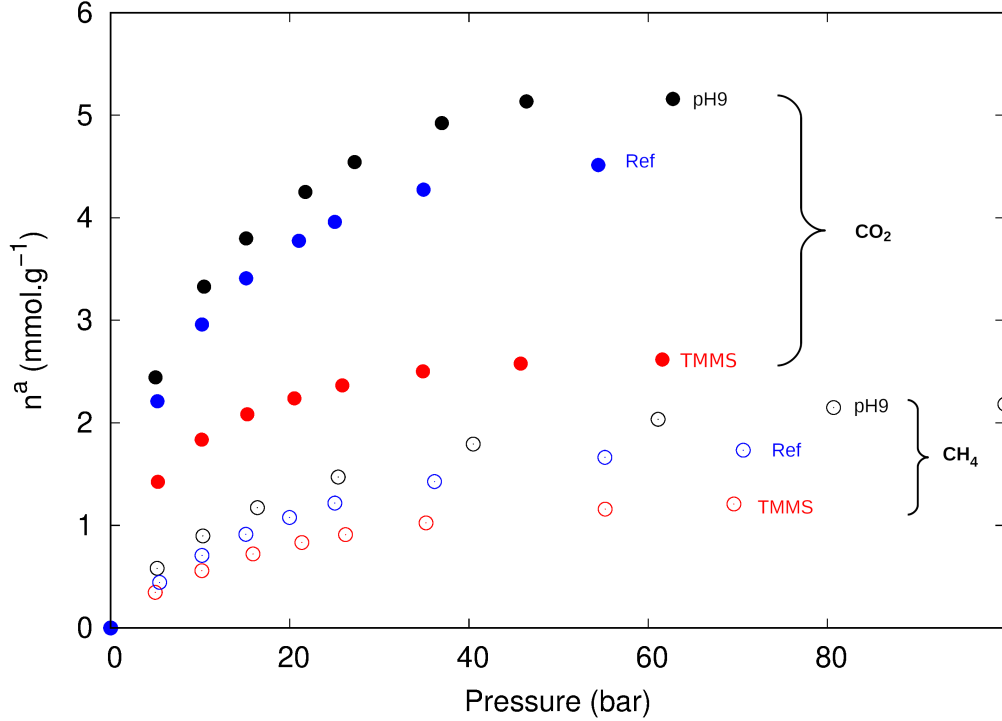


Figure 5: **Methylation reduces adsorption capacity for both pure gases.** Adsorption isotherms of pure CO<sub>2</sub> (●) and pure CH<sub>4</sub> (○) for the  $S_{\text{ref}}$  (blue),  $S_{\text{pH9}}$  (black) and  $S_{\text{TMMS}}$  silicas (red). Capacity for CO<sub>2</sub> relative to CH<sub>4</sub> is greater at lower pressure, see Table 2.

Silica material	$R_{5 \text{ bar}}$	$R_{55 \text{ bar}}$
$S_{\text{ref}}$	5	2.7
$S_{\text{pH9}}$	4.1	2.2
$S_{\text{TMMS}}$	4.2	2.5

Table 2: **Greater CO<sub>2</sub> than CH<sub>4</sub> adsorption at low pressure by  $S_{\text{ref}}$ .** The ratio of the amounts adsorbed from either gas separately,  $R_p = n_{\text{CO}_2}^a / n_{\text{CH}_4}^a$ , cf. Fig. 5 for  $S_{\text{ref}}$ ,  $S_{\text{pH9}}$  and  $S_{\text{TMMS}}$  at low and high pressure.

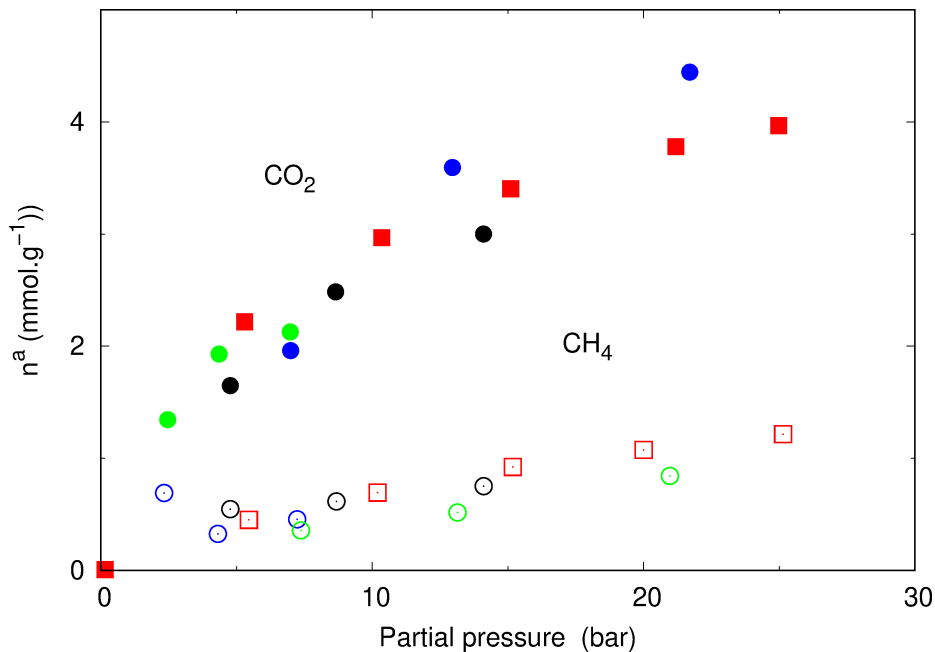


Figure 6: **Silica  $S_{\text{ref}}$  is CO<sub>2</sub>-selective.** Specific adsorbance ( $n^a$ ) of CO<sub>2</sub> exceeds that of CH<sub>4</sub>, even from CH<sub>4</sub>-rich mixtures. Simultaneous adsorption isotherms of CO<sub>2</sub> (●) and CH<sub>4</sub> (○) from CO<sub>2</sub>/CH<sub>4</sub> gas mixtures in the proportions: 25/75 (green), 50/50 (black) and 75/25 (blue) v/v; red squares: pure gases (*cf.* Fig. 5).

$S_{\text{ref}}$ . The plot of specific adsorptions,  $n_a$ , against partial pressures in Fig. 6 shows that to within experimental accuracy the amounts adsorbed depend only on the partial pressures, with significant selection of CO<sub>2</sub>.

Fig. 7 shows another common way of representing selective adsorption, the separation factor,

$$SF = \frac{x_{\text{CO}_2}/x_{\text{CH}_4}}{y_{\text{CO}_2}/y_{\text{CH}_4}}, \quad (2)$$

where  $x_i$  is the molar fraction of adsorbed species  $i$  and  $y_i$  the molar fraction in the equilibrated gas above the adsorbent, see the SI. Material  $S_{\text{ref}}$  achieves high SF for CO<sub>2</sub> *vs.* CH<sub>4</sub> at compositions representative of raw biogas *e.g.* CO<sub>2</sub> fraction between and 10 and 50 % and pressure under 20 bar.

Therefore, the best compromise between the adsorption capacity and the separation factor is obtained for a CO<sub>2</sub> composition below 30% and a pressure below 20 bars. The adsorption capacity of CO<sub>2</sub> can then be as high as

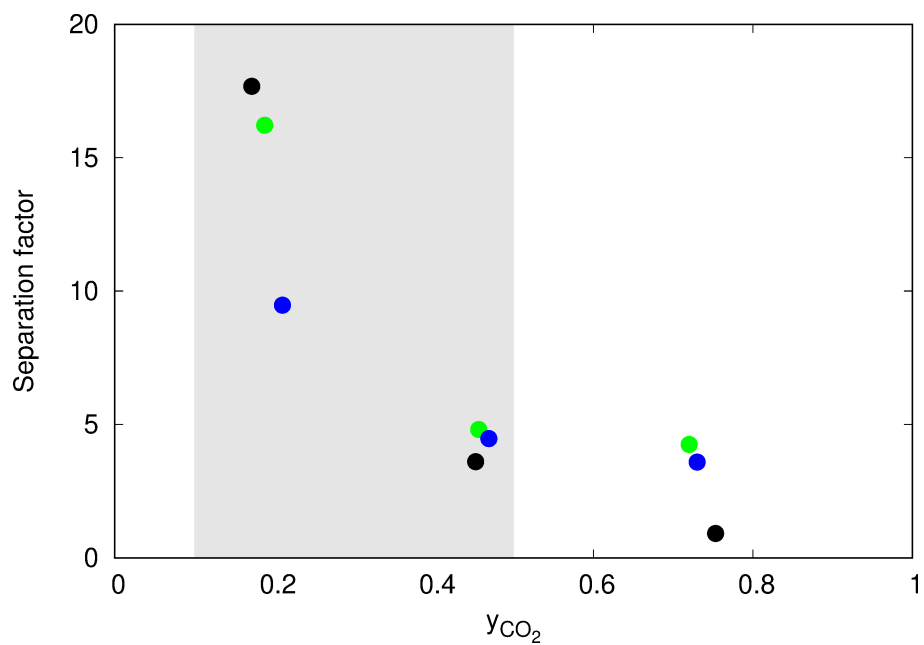


Figure 7: **Efficient separation ability especially at low CO<sub>2</sub> content and moderated pressures.** Separation factors of  $S_{\text{ref}}$  vs. the gas phase fraction of CO<sub>2</sub> for 3 different pressures. 10 bar (black), 17 bar (green) and 28 bar (blue). Grey rectangle: typical biogas application range.



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Adsorbant	CO <sub>2</sub> /CH <sub>4</sub> adsorption mmol.g <sup>-1</sup>	Selectivity	Experimental conditions	Type of porosity
Present work, $S_{\text{ref}}$	2.8 / 0.7	4	10 bars, 303K	Micro-
NaX Zeolite[35]	6 / 3.2	1.9	1 bar, 303K	Micro-
MAXSORB-III[36]	10 / 5.6	1.8	1 bar, 300K	Meso-
5A Zeolite[37]	3.6 / 2	1.8	10 bar, 303K	Micro-
AC ROx 0.8 [38]	4 / 1.6	2.5	10 bar, 303K	Micro-
MCM-41[39]	4.5 / 1.2	3.7	1 bar, 298K	Meso-
MOF-200/GO [40]	1.34 / 0.20	6.7	1 bar, 298K	Micro-meso-macro
MMM SSZ-16 [41]	2.28 / 0.35	6.5	1 bar, 298K	Micro-
K-Rho Zeolite[42]	3.7 / 0.04	92	10 bar, 298K	Meso-

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Table 3:  $S_{\text{ref}}$  combines moderate adsorption capacity and good selectivity in an easily synthesised and cheap material compared to well-known ones. Comparison of  $S_{\text{ref}}$  with materials commonly used to separate CO<sub>2</sub> and CH<sub>4</sub>.

2.8 mmol.g<sup>-1</sup> vs. only 0.7 mmol.g<sup>-1</sup> for CH<sub>4</sub>, and the separation factor can exceed 15. While several materials in the literature perform better for one or other metric, *e.g.* MOF-200/GO for selectivity but not for adsorption capacity, or MAXSORB-III for the reverse combination, see table 3,  $S_{\text{ref}}$  combines here moderate adsorption capacity and fair to high selectivity in an easy, cheap synthesis, not the case for MMM SSZ-16 for example.

### 3. Conclusion

The present easy and cheap sol-gel synthesis leads to microporous to mesoporous amorphous silica materials with different water affinity, aimed here at CO<sub>2</sub>/CH<sub>4</sub> separation. They were characterized by several experimental techniques in order to establish their composition, porosity and water content, specially free and bound water and rehydration kinetics.

The mesoporosity and possibly the slightly higher surface density of hydroxyls in  $S_{\text{ph9}}$  lead to greater CO<sub>2</sub> adsorption capacity, but at the expense of selectivity which is greatest in microporous  $S_{\text{ref}}$ , which attains a selectivity of 4 and a separation factor over 15 in CO<sub>2</sub>-poorer CO<sub>2</sub>/CH<sub>4</sub> mixtures at low pressures. Contrary to expectation, we find a degree of residual water in  $S_{\text{ref}}$  is favorable to CO<sub>2</sub> adsorption at higher pressures. Thus, peak adsorption of CO<sub>2</sub> requires only moderate heating (80 °C) to drive off atmospheric and residual synthesis water before use or to regenerate the material. Furthermore, rehydration under ambient conditions is slow, some hours. Considering the facile and cheap synthesis, the material thus appears promising for applications like natural gas sweetening or biogas upgrading.

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## Highlights

### **CO<sub>2</sub> capture and CO<sub>2</sub>/CH<sub>4</sub> separation by silicas with controlled porosity and functionality**

Saphir Venet, Frédéric Plantier, Christelle Miqueu, Ali Shahtalebi, Ross Brown, Thierry Pigot, Patrice Bordat

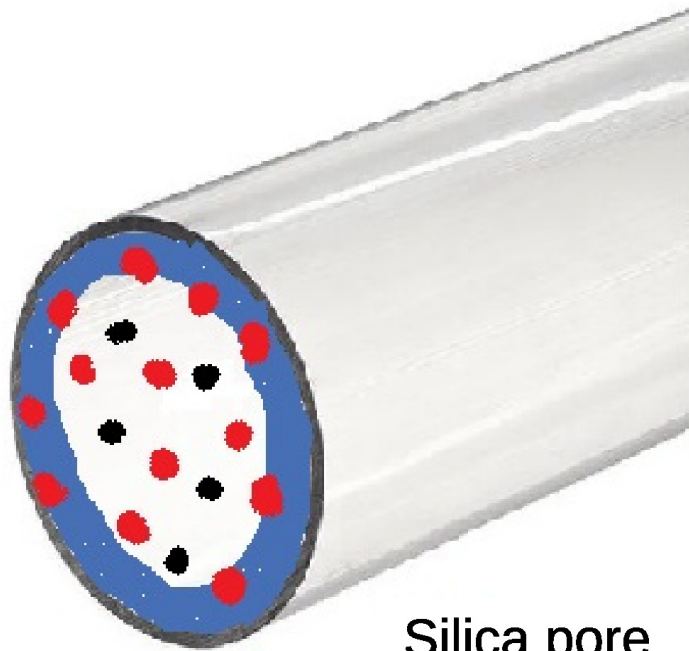
- Porous silicas with both controlled hydrophilicity and micro-/mesoporosity.
- Materials exhibiting a high separation factor (SF), favouring CO<sub>2</sub> relative to CH<sub>4</sub>.
- Degree of residual water favours CO<sub>2</sub> adsorption.
- Easy and cheap one-pot synthesis.
- Gas physisorption favours low cost regeneration.
- Optimal use at low pressures and low CO<sub>2</sub> content.



+  $\text{CO}_2/\text{CH}_4$   
mixture



Residual  
water



●  $\text{CO}_2$   
●  $\text{CH}_4$

Silica pore

