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Amino functionalised Silica-Aerogels for CO_2-adsorption at low partial pressure

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Abstract Effective adsorption of CO_2 at low partial pressures is required for many technical processes, such as gas purification or CO_2 removal in closed loop environmental control systems. Since the concentration of CO_2 in such applications is rather low, a high adsorption capacity is a required property for the adsorbent. Silica aerogels possessing an open pore structure, a high porosity and a high surface area, have a great potential for utilisation as CO_2 adsorbents. Nonetheless in order to reach high adsorption capacities, silica aerogels should be functionalised, for instance by amino functionalisation. In this work, two different functionalisation methods were applied for the generation of amino functionalised aerogels: co-condensation during the sol-gel process and post-treatment of the gel. The co-condensation functionalisation allows the introduction of up to 1.44 wt.% nitrogen into the aerogel structure with minor reductions in surface area, leading however only to minor increases in the adsorption capacity at low partial pressures. The post functionalisation of the gel causes a greater loss in surface area, but the CO_2 adsorption capacity increases, due to the introduction of higher amounts of amino groups into the aerogel structure (up to 5.2 wt.% nitrogen). Respectively, 0.523 mmol CO_2/g aerogel could be adsorbed at 250 Pa. This value is comparable with the adsorption capacity at this pressure of a standard commercially available adsorbent, Zeolite 13X.

Keywords Carbon dioxide adsorption · Silica · Aerogel · Amino functionalisation · Zeolite 13X · Low partial pressure

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1 Introduction

Closed loop environmental control systems (CL-ECS) are applied in spacecrafts (Knox 2000) and submarines (Satyapal et al. 2001) for the removal of CO_2 from these enclosed inhabited environments. They also have a high potential for increasing the fuel efficiency and cabin air quality in aircraft. With the integration of a closed loop environmental control system in an aircraft the energy for conditioning outside air at aircraft cruise altitude from outside pressure to cabin pressure can be saved and the moisture content of the ventilation air can be increased. To remove the passenger-emitted CO_2 accumulating in the recirculated air a CO_2 removal unit has to be applied. The application of an adsorption system for CO_2 removal is promising, because the adsorption process promises to consume less energy in sorbent regeneration in comparison to absorption processes (Plaza et al. 2009). The effectiveness of an adsorption process highly depends on the properties of the adsorbent (Harlick and Tezel 2004), which should possess a high capacity for adsorbing CO_2 at low partial pressures (Serna-Guerrero et al. 2010) to reduce the weight of the adsorption system. The CO_2 concentration in the aircraft should not exceed 2500 ppm (250 Pa) and the adsorbent should cope with moist air. At the same time the weight and the pressure drop of the system should be minimized.

Silica aerogels, possessing an open pore structure, a high porosity and surface area can be successfully used as an adsorbent for the purification of polluting gases (Santos et al. 2008). However, their CO_2 adsorption capacity at low partial pressure is too small for the efficient utilization in a CO_2 removal system. Since liquid amines have been traditionally used for selectively removing of CO_2 from various process streams in absorption processes, one promising way for the improvement of the CO_2 adsorption capacity of silica materials is the incorporation of aminosilanes into the silica structure. This has been shown for silica gels by many research groups with various aminosilanes (Leal et al. 1995; Franchi et al. 2005; Serna-Guerrero et al. 2010; Belmabkhout et al. 2010). The effect of aminosilanes on the properties of aerogels has been investigated by Hüsing et al. (1999). Functionalisation of aerogels with amino groups was used for improving their strength and elasticity (Katti et al. 2006; Meador et al. 2005; Capadona et al. 2006). Amino groups have also been reported to improve the adsorption of pharmaceutics (Alnaief and Smirnova 2010) and copper (Im et al. 2000) in aerogels. Santos et al. (2008) used amino functionalised aerogels combined with wollastonite for CO_2 adsorption and storage. In these samples CO_2 is not bound by the amino groups but by the formation of carbonate to the aerogel. Cui et al. (2011) achieved a CO_2 adsorption capacity of 6.97 mmol/g at 25 °C in moist conditions (10 % CO_2 and 10 % H_2O) with a post functionalised aerogel with a nitrogen content of 3.91 wt.% and a surface area of 628 m^2/g. In this work the methods from Alnaief and Smirnova (2010) are adopted for improving the CO_2 adsorption capacity of silica aerogels.

Regarding the adsorption mechanism of CO_2 on primary amines, one mole of CO_2 is adsorbed by two moles of amines in the absence of water.

$$2\,RNH_2 + CO_2 \leftrightarrow RNH_3^+ + RNHCOO^- \tag{1}$$

The aim of this work is the investigation of the influence of amino functionalisation methods on the CO_2 adsorption properties of aerogels at low partial pressure. Two different methods for the introduction of aminosilanes into the aerogel structure were compared in terms of CO_2 adsorption capacities and structural properties of the resulting material: co-condensation in the sol-gel process and post-treatment of the gel. Finally, the best produced aerogel is compared to the state of the art commercial adsorbents Zeolite 13X, an amino functionalised silica gel and alkaline activated carbon.

2 Material and methods

2.1 Materials

All materials used in this work are commercially available. The suppliers are listed in Table 1.

Table 1 Chemicals and suppliers

Zeolite 13X	Sigma Aldrich	Germany
Aminofunct. silica gel	Sigma Aldrich	Germany
Alkaline activated carbon	Draeger	Germany
TMOS 98 %	Fluka	Germany
APTMS 97 %		
Methanol 99.5 %	Merck	Germany
HCL 30 %		
Ammonia hydroxide (25 %)		
CO_2 (sc drying)	AGA Gas	Germany
CO_2 (isotherm measurement)	Westfalengas	Germany

2.2 Characterisation of samples

Pure component adsorption was measured with a Nova 3200e (Quantachrome) modified for multi-gas adsorption. The CO_2 adsorption isotherms were measured at 273 K with pure CO_2 (Zhang et al. 2008; Vaidhyanathan et al. 2009; Tang and Landskron 2010). For this purpose 0.1–0.4 g of sample were used and prepared by outgassing at 80 °C in vacuum for 16 h. The equilibration time for the CO_2 adsorption measurements was 120 s and the equilibration timeout was 240 s. The isotherm measurements were conducted in triplicates and fitted by Freundlich equation.

The temperature swing experiments were conducted in a laboratory scale adsorption column, with an adsorber bed length of 0.3 m ($V = 150$ ml). The mass of adsorbents was 14.29 g and its Sauter mean diameter was 1 mm. The breakthrough curves of CO_2 (2500 ppm) in air/CO_2 mixtures were measured at 22 °C and the total pressure of 1 bar. The gas flow rate was 1 Nl/min. The desorption was conducted at ambient pressure, with nitrogen flow at 70 °C.

The nitrogen adsorption—desorption tests were carried out at 77 K in a Nova 3200e (Quantachrome) after 16 h of sample outgassing in vacuum. ATR-IR experiments were performed with an Alpha P (Bruker). CHN analysis was performed with a Carlo Erba EA 1108 Elemental analyzer in duplicates.

2.3 Functionalisation methods

Silica aerogels used in the present work were produced by a two-step process using tetramethylorthosilicate (TMOS) as precursor (Smirnova and Arlt 2003). The TMOS was hydrolysed in a first step and polymerised to a stable gel in the second step. Two methods of functionalisation were applied to introduce the aminosilane ((3-Aminopropyl)trimethoxysilane (APTMS)) into the aerogel structure (Alnaief and Smirnova 2010). The first one introduced the APTMS into the aerogel structure by post functionalisation of the gel and the second one by co-condensation (cc).

2.4 Post-functionalisation

The post-functionalised aerogels were prepared by a modification of the two step method. The first step consists of the mixing of: 1 mol TMOS: 2.4 mol methanol: 1.3 mol water: 10^{-5} mol hydrochloric acid. This sol was stirred at room temperature for 30 minutes. Then in the second step ethanol was added to produce the desired density and additional water and ammonia solution were added to produce a gel with the final molar ration of: 1 mol TMOS: 2.4 mol methanol: 4 mol water: 10^{-5} mol hydrochloric acid: 10^{-2} mol ammonia. These gels were aged for 48 h in ethanol. The produced gels were then put into an ethanol/APTMS solution and stored for a defined time (24–48 h) at 50 °C, for the APTMS to bond to the surface of the gel. The volumetric ratio of the aerogel to the ethanol/APTMS solution was 1:2. Afterwards the gels were washed with ethanol and prepared for supercritical drying in CO_2. The samples of this functionalisation method are labelled after the concentration of APTMS in the functionalisation solution and their target density (e.g.. 2 % 0.08).

The post functionalisation method was combined with the emulsion method for the production of aerogel particles by Alnaief and Smirnova (2011) on the set of experiments for the temperature swing adsorption behaviour. Prior to the functionalisation step the oil from the emulsion was separated from the aerogel by washing. Apart from the differences in the gelation step the rest of the production of the aerogel particles is similar to that reported before.

2.5 Functionalisation by co-condensation (CC)

For the cc-functionalisation method ammonia hydroxide was replaced by a varying amount of APTMS to catalyse the gelation. The solution for the first and second step were mixed separately and cooled down before merging to 273 K to slow down the gelation. The first step consists of the mixing of: $1 - x$ mol TMOS: 2.4 mol methanol: 1.3 mol water: 10^{-5} mol hydrochloric acid. This sol was stirred at room temperature for 30 minutes before being cooled down. In the second step ethanol was used to reach the desired density and additional water and APTMS were added to produce a final molar ratio of: $1 - x$ mol TMOS: 2.4 mol methanol: 4 mol water: 10^{-5} mol hydrochloric acid: x mol APTMS. This solution was also cooled down before being mixed with the solution of step 1. The mixture was poured into cylindrical flasks. The cylindrical gels produced in this way were then supercritically dried with CO_2 after 48 h of aging in ethanol. The samples of this functionalisation method are named by their target density and their APTMS content in relation to the content of TMOS (e.g. 0.08 2 % would correspond to a sample with a target density of 0.08 g/cm^3, whereas a mixture of APTMS and TMOS used for the sol preparation contains 2 wt.% of APTMS and 98 wt.% TMOS).

3 Results and discussion

3.1 Nitrogen content of the produced aerogels

Tables 2 and 3 display the surface area and the nitrogen content of the produced aerogels. In addition the nitrogen yield, being the measured nitrogen content of the functionalised aerogels divided by the theoretical nitrogen content, is presented. One mole of nitrogen corresponds to one mole of APTMS (one amino group) in the aerogel sample, since no other nitrogen sources are present in the system. The produced samples of functionalised aerogel show similar mechanical properties compared to non functionalised silica aerogels produced by this method.

In case of cc-functionalisation (Table 2) APTMS can be bounded into the aerogels up to a limit of ca. 1.44 wt.% of nitrogen in the aerogel. Higher concentrations of APTMS do not show any considerable increase in the nitrogen content inside the aerogel. The very fast gelation of the gel with high APTMS content may cause the incomplete incorporation of the APTMS into the gel. The fast gelation results from the significant increase of the pH values due to the addition of the amino group (Hüsing et al. 1999). The fact that more nitrogen than the theoretically possible amount is incorporated into the aerogel structure for the samples with lower APTMS concentrations may result from incomplete TMOS conversion during gelation as also reported by Hüsing et al. (1999). Nitrogen adsorbed from air should not increase nitrogen contents significantly since amino functionalised silica materials are reported to have a negligible N_2 adsorption capacity (Serna-Guerrero et al. 2010). The amount of amino groups inside the aerogels might be further increased by using a lower temperature or via pH control during the gelation. Hüsing et al. (1999) report over 80 % of the APTMS introduced into silica aerogels at a high initial rate of up to 43 % APTMS incorporated into the tetraethylorthosilicate aerogel. These aerogels were produced by a one-step method in contrast to the two-step method used in this work.

The post functionalised aerogels (Table 3) exhibit higher absolute nitrogen contents, but a lower nitrogen yield, resulting from the incomplete incorporation of the APTMS. The observation of an incomplete incorporation of the APTMS into the aerogel structure is also made by Alnaief and Smirnova (2010) and Bois et al. (2003). Alnaief and Smirnova (2010) report similar nitrogen concentrations in the functionalised aerogels. Bois et al. (2003) reports a nitrogen yield of 80 % at 2.5 wt.% nitrogen incorporated into the aerogel, which is comparable to our observations. The increase in nitrogen content can be described by a nonlinear function of APTMS concentration in the solution, being steep at lower APTMS concentrations and flat at higher ones. The time for post functionalisation is varied between 24 h and 48 h, whereas the longer functionalisation time results in higher nitrogen contents (Table 3).

In general, one can conclude that at given conditions the post functionalisation is the method of choice to achieve high nitrogen content in the aerogels, which promises to be more favourable for CO_2 adsorption. However, further investigations of the influence of the nitrogen content on the

Table 2 Surface area and nitrogen content of cc-functionalised aerogels

Sample	BET Surface area [m^2/g]	Nitrogen content [wt.%]	Nitrogen yield [%]
0.08 2 %	946 (±47)	0.46 (±0)	1.28
0.08 5 %	919 (±46)	0.90 (±0.04)	1.05
0.08 8 %	919 (±46)	1.49 (±0)	1.15
0.08 20 %	741 (±37)	1.40 (±0.01)	0.51
0.1 2 %	950 (±48)	0.46 (±0.01)	1.28
0.1 5 %	800 (±41)	0.84 (±0)	0.99
0.1 8 %	832 (±42)	1.42 (±0.01)	1.09
0.1 20 %	709 (±35)	1.44 (±0.02)	0.52

Table 3 Surface area and nitrogen content of post-functionalised aerogels

Sample	Functionalisation time [h]	BET Surface area [m^2/g]	Nitrogen content [wt.%]	Nitrogen yield [%]
0.08 2 %	24	673 (±34)	2.80 (±0.17)	0.76
0.08 2 %	48	678 (±34)	3.11 (±0.32)	0.85
0.08 5 %	24	558 (±28)	4.53 (±0.03)	0.76
0.08 5 %	48	520 (±26)	5.50 (±0.28)	0.92
0.08 8 %	24	607 (±30)	4.63 (±0.04)	0.65
0.08 8 %	48	588 (±29)	4.76 (±0.04)	0.66
0.08 20 %	24	532 (±27)	5.02 (±0.06)	0.57
0.08 20 %	48	463 (±23)	5.08 (±0.03)	0.58
0.1 2 %	24	828 (±41)	2.59 (±0.98)	0.82
0.1 2 %	48	904 (±45)	2.3 (±0.55)	0.73
0.1 5 %	24	629 (±32)	2.15 (±0.13)	0.40
0.1 5 %	48	796 (±40)	4.42 (±0.15)	0.82
0.1 8 %	24	573 (±29)	4.70 (±0.04)	0.71
0.1 8 %	48	583 (±29)	4.80 (±0.01)	0.73
0.1 20 %	24	570 (±29)	5.16 (±0.03)	0.61
0.1 20 %	48	633 (±32)	5.19 (±0.04)	0.61

surface area and on the CO_2 adsorption capacity have to be conducted.

3.2 Surface area of the produced aerogels

CO_2 adsorption is generally influenced not only by the content of amino groups but also by the surface area of the adsorbent itself. Figure 1 shows that the surface area for the produced aerogels decreases with increasing nitrogen content for both functionalisation methods. The results for the single aerogel samples are presented in Tables 2 and 3. Non functionalised silica aerogels exhibit a surface area of 1000 m^2/g, a value that is not reached by the functionalised aerogels. The trend of decreasing surface area with increasing nitrogen content in the cc-functionalisation may be caused by the fast gelation and incomplete formation of the silica network. For cc-functionalised aerogels Hüsing et al. (1999) report an increase in surface area with increasing nitrogen content until a maximum is reached (426 m^2/g) at a nitrogen concentration of 4.3 wt.%. Bois et al. (2003) confirms the trend of a decreasing surface area with increasing nitrogen content for cc-functionalised gels, reporting a reduction in surface area from 700 m^2/g for non functionalised silica gels to 62–65 m^2/g for silica gels with 2.5 wt.% nitrogen. The observed surface areas from these publications are generally lower compared to the ones in this study.

The decrease in surface area at increasing nitrogen concentrations is also reported for the post functionalisation method by Clavier et al. (2005) and Alnaief and Smirnova (2010). Harlick and Sayari (2007) report a similar trend for post functionalised MCM 41 silica gels. The trend may be induced by pore blocking of the grafted APTMS molecules.

3.3 CO_2 adsorption isotherms of single sets of aerogels

In this section the CO_2 adsorption isotherms for two sets of functionalised aerogels are compared to the isotherm of an

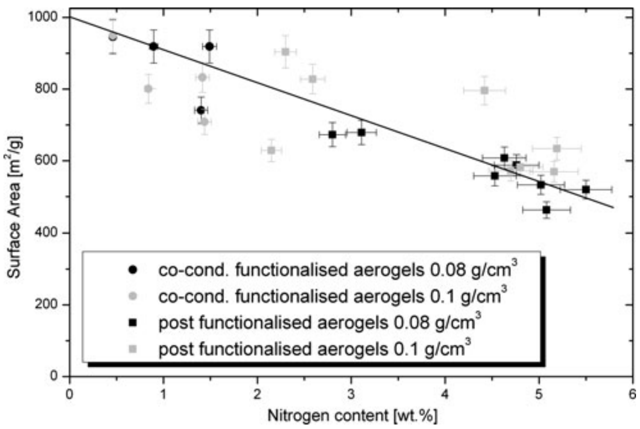

Fig. 1 Nitrogen content and surface area of cc functionalised and post-functionalised aerogels. Surface area of unfunctionalised aerogel 1000 m^2/g. Line is a guide for the eye

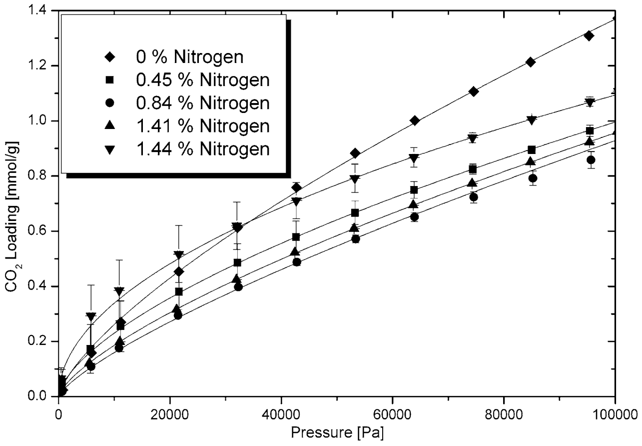

Fig. 2 CO_2 adsorption isotherms of cc functionalised aerogels, $\rho = 0.1$ g/cm^3

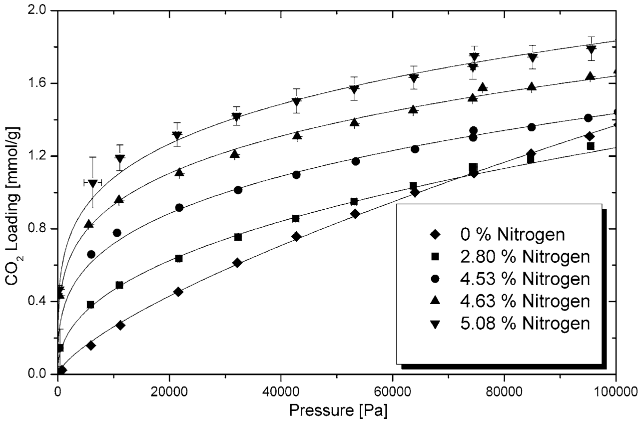

Fig. 3 CO_2 adsorption isotherms of post-functionalised aerogels, $\rho = 0.1$ g/cm^3

unmodified aerogel (1000 m^2/g) of the same density. Figure 2 displays the adsorption isotherms of cc-functionalised aerogels and Fig. 3 the isotherms of post functionalised aerogels.

The CO_2 adsorption results of the cc-functionalisation (Fig. 2) show that this adsorption method is not suitable for increasing the adsorption capacity for most of the produced aerogels. The only exception is the sample with the highest nitrogen content (1.44 wt.%), which shows an increase in adsorption capacity at low CO_2 partial pressures in comparison to the non functionalised aerogel. For most samples the amount of amino groups in the produced aerogels is too low for enhancing the adsorption capacity. Nonetheless, the difference between the nitrogen content of the sample with the highest nitrogen content (1.44 wt.%) and the nitrogen content of the sample with the second highest nitrogen content (1.40 wt.%) do not justify the difference in the adsorption behaviour. Hence, further investigations for example on the availability of the amino groups on the surface of the aerogel have to be performed. However, currently this method does not seem to be useful for the production of aerogels for CO_2 adsorption applications.

The post functionalised aerogels (Fig. 3) show an increase in CO_2 adsorption capacity with increasing nitrogen content for all samples, especially at low partial pressures.

Comparing these results with Tang and Landskron (2010), the trend of increasing CO_2 adsorption capacity with increasing nitrogen concentration despite lower surface area is confirmed. The decrease in surface area was even more significant in the study by Tang and Landskron (2010) dropping from 735 m^2/g to 38 m^2/g. On the other hand, the maximum CO_2 adsorption capacity increases from 1.36 $mmol_{CO_2}/g$ to 2.27 $mmol_{CO_2}/g$ at 10^5 Pa despite the decrease in surface area.

3.4 Influence of nitrogen content on CO_2-loading at 250 Pa

The CO_2 loading at low pressures is an important factor for the application of the functionalised aerogels in CO_2 adsorption processes. Therefore the effect of the nitrogen content on CO_2 adsorption at one fixed pressure (250 Pa) is presented in Fig. 4. The trend of increasing CO_2 loading at increasing nitrogen content, as reported in the previous section, accounts for all post functionalised samples. The cc-functionalised aerogels containing small proportions of nitrogen exhibit a low CO_2 loading despite possessing a high surface area, as shown in Fig. 1. The trend of increasing CO_2 adsorption capacity at increasing nitrogen concentrations is not evident with this functionalisation method as discussed before. The content of amino groups in the aerogels may not be sufficient to increase the CO_2 adsorption capacity.

Comparing these results to adsorption measurements by Franchi et al. (2005) and Harlick and Sayari (2006) at

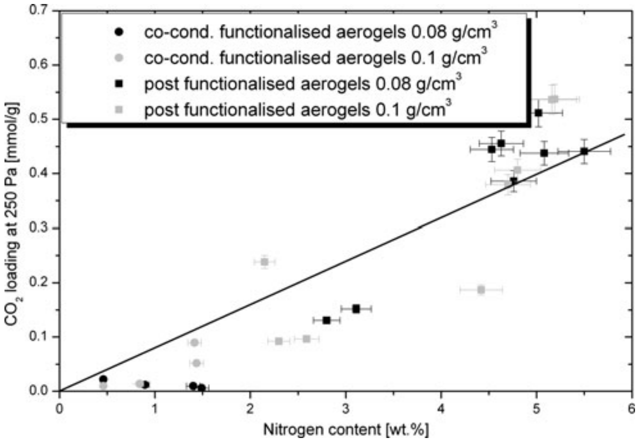

Fig. 4 CO_2 adsorption at 250 Pa as a function of the aerogels nitrogen content. Line is a guide for the eye

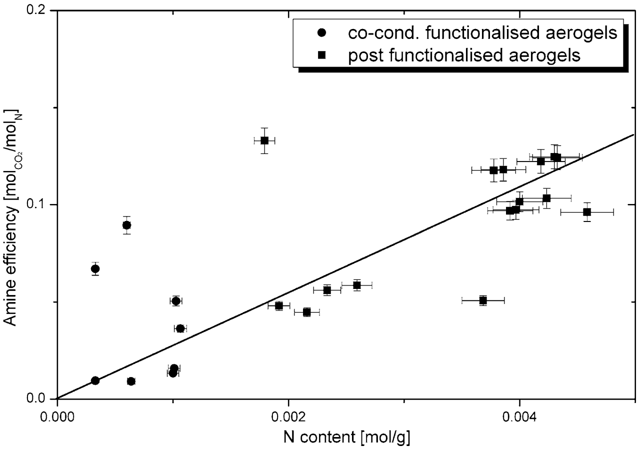

Fig. 5 Amine efficiency at 250 Pa. Mol_{CO_2} adsorbed per mol nitrogen versus the nitrogen content of the samples. Line is a guide for the eye

5000 Pa CO_2 partial pressure in nitrogen with di- and triamine functionalised MCM 41 silica gels, the trend of increasing CO_2 adsorption capacity with increasing nitrogen content is expectable.

3.5 Adsorption efficiency of the amino groups

To investigate whether all amino groups are involved in adsorbing CO_2, the results are presented as mole of CO_2 adsorbed per mol N in the aerogel (amine efficiency) versus the nitrogen content of the aerogels in Figs. 5 and 6. At a low CO_2 pressure of 250 Pa, as shown in Fig. 5, the trend of an increase in amine efficiency at higher nitrogen concentrations is observed. Based on the theory of CO_2 binding to amino groups in dry conditions one mole of CO_2 should be adsorbed by two moles of amine (Serna-Guerrero et al. 2010). Hence, with an increasing density of amino groups per surface area it is more likely that two amino groups can work together to adsorb one CO_2 molecule. But the maximum ratio of CO_2 adsorbed per mol_N is below the theoretical value. This can be explained by the fact that not all amino groups might be available for adsorption due to pore blocking, reactions with the surface of the aerogel or intra molecular bondings.

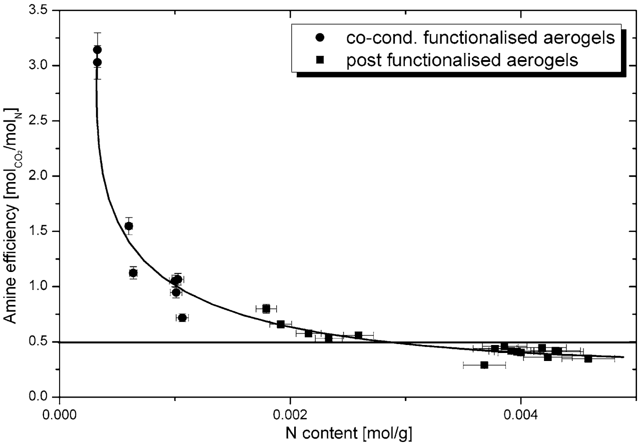

Fig. 6 Amine efficiency at 10^5 Pa. Mol CO_2 adsorbed per mol nitrogen versus the nitrogen content of the samples. Lines are a guide for the eye. 0.5 is the theoretical amine efficiency as defined in the manuscript

Franchi et al. (2005) also report an increasing amine efficiency starting for modified MCM 41 silica gels from low concentrations until a maximum is reached at a nitrogen concentration of 8 wt.%. Harlick and Sayari (2006, 2007) report similar results from a modified MCM 41 silica gel. The results indicate that a certain density of amino groups per surface area is necessary to adsorb the CO_2 effectively.

At high CO_2 pressures (10^5 Pa) the ratio of the mol CO_2 adsorbed per mol nitrogen declines with increasing nitrogen content (Fig. 6). However, with increasing nitrogen content this influence is reduced until ratios below the theoretical limit of 0.5 mol_{CO_2} per mol_N are achieved. This trend may be explained for CO_2 adsorption to the hydroxyl groups on the surface, since all the amino groups are already loaded at this pressure. At high nitrogen contents not all amino groups might be available for the CO_2 adsorption, due to pore blocking.

3.6 ATR-IR measurements

The results of the ATR-IR measurements are presented in Fig. 7. The displayed samples are the unmodified 0.1 Si-aerogel, the 0.1 20 % cc-functionalised aerogel and the 0.1 48 h 20 % post-functionalised aerogel. Significant differences are observed between the functionalised aerogels and the non functionalised ones. The unmodified silica aerogel exhibits a clearly visible peak at 968 cm^{-1} indicating the Si-OH (silanol) groups in the aerogel. This peak is less pronounced for the functionalised aerogels, indicating less OH groups in the functionalised samples. The absence of

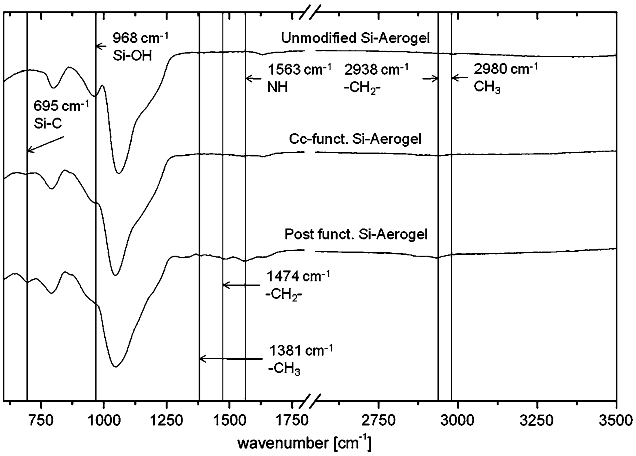

Fig. 7 ATR-IR measurements of unmodified Si-Aerogel, cc-functionalised Si-Aerogel (0.1, 1.5 wt.% Nitrogen) and post functionalised Si-Aerogel (0.1, 48 h, 5.2 % Nitrogen)

CH_3 bonds at 1381 cm^{-1} and 2980 $cm^{-1}$for the non functionalised aerogel indicates the complete hydrolysis of the TMOS and the complete ethanol removal during supercritical drying. The Si-C bonds in the functionalised samples can be attributed to the addition of the APTMS into the aerogel structure. Additionally, CH_2 peaks at 1474 cm^{-1} and at 2938 cm^{-1} also confirm the successful incorporation of the APTMS into the aerogel structure (Cui et al. 2011). Finally, the visible peak at 1563 cm^{-1} is attributed to the NH group for the both functionalised aerogels. All peaks indicating the incorporation of the APTMS into the silica structure of the aerogel are more pronounced for the post functionalised aerogel as for the cc-functionalised aerogel. These results are in accordance to the result of the nitrogen measurements.

3.7 Temperature swing adsorption

To investigate the desorption conditions of the functionalised aerogels temperature swing adsorption experiments were conducted with post functionalised silica aerogel particles. The results of the breakthrough experiments are presented in Figs. 8 and 9. Fig. 8 shows that the time needed for adsorption until saturation was similar to the time needed for desorption at 70 °C, indicating good desorption kinetics. Fig. 9 shows a constant breakthrough and saturation loading for the aerogel adsorbent at these conditions for 4 experiments. The aerogels exhibit similar breakthrough and saturation loadings in these experiments. Hence, the post functionalised aerogels could be regenerated at 70 °C in a nitrogen flow. The observed desorption temperature is similar to the 75 °C observed by Serna-Guerrero et al. (2010) for a regeneration of post functionalised MCM-41 silica gel. Leal et al. (1995) reported a higher desorption temperature of around 100 °C for their amino functionalised silica gel.

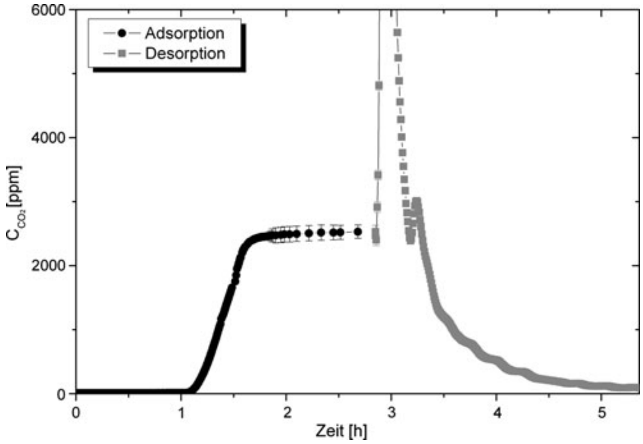

Fig. 8 CO_2 concentration at outlet of adsorber of temperature swing experiment at flow of 1 Nl/min and 1 bar, 2500 ppm CO_2. Aerogel properties: 5.7 wt.% nitrogen content, 200 m^2/g surface area. Adsorption at 22 °C and desorption at 70 °C

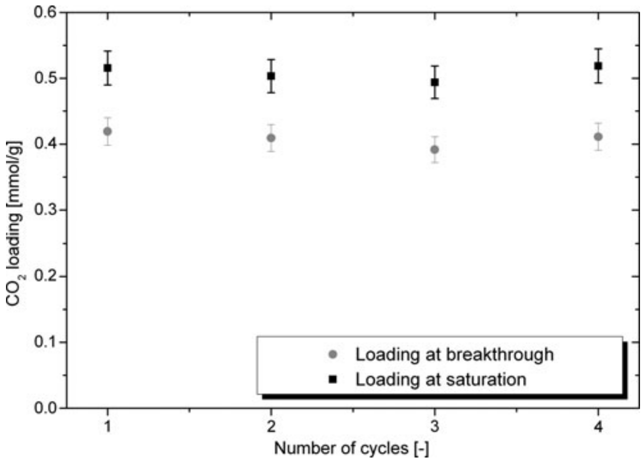

Fig. 9 Saturation and breakthrough loading of the temperature swing experiments

3.8 Comparison of post functionalised aerogel with other adsorbents

In this section the functionalised aerogels are compared with commercial available adsorbents in terms of the CO_2 adsorption capacity. For this purpose the adsorption isotherms of an alkaline activated carbon, the Zeolite 13X and an amino functionalised silica gel were compared in Fig. 10 to the best post functionalised aerogel. The nitrogen content of the silica gel is 1.2 wt.% and the surface area 550 m^2/g, which is lower compared to the post functionalised aerogel. This can explain the low CO_2 adsorption capacity of this material. The adsorption capacity of the alkaline activated carbon is also low at low partial pressures in comparison to the aerogel. The only material showing comparable adsorption capacity to the selected post functionalised aerogel (5.2 wt.% nitrogen, 48 h) at low partial pressures is the Zeolite 13X.

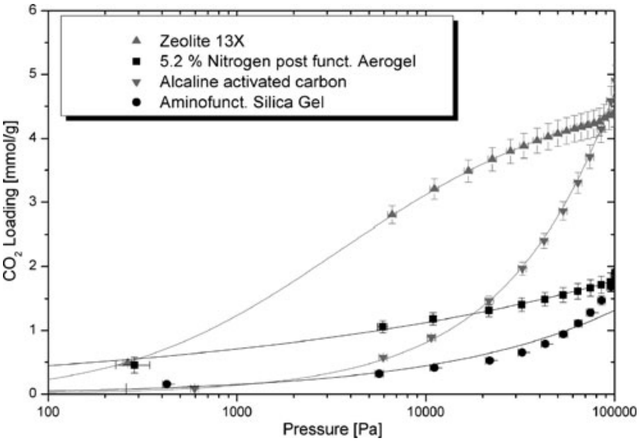

Fig. 10 Comparison of commercial adsorbents and the post-functionalised aerogel (sample 0.1 20 % 48 h, nitrogen content 5.2 wt.%)

For gas purification processes at these low partial pressures not only the CO_2 adsorption capacity itself, but also other characteristics of the materials are important. The air from enclosed inhabited environments also contains a significant amount of humidity. Zeolites show preferable water adsorption, hence their CO_2 adsorption capacity is greatly reduced by moisture (Belmabkhout et al. 2010). Because of this, zeolites demand for additional desiccant beds in adsorption processes, like used in the International Space Station (Knox 2000). These desiccant beds enlarge the overall weight, pressure drop and complexity of the CO_2 removal system. The adsorption capacity of the amino functionalised aerogels should not be affected by moisture. In contrary, the molar adsorption capacity of the amino group should be doubled in presence of moisture (Franchi et al. 2005). Corresponding investigations for amino functionalised aerogels are currently carried out in our group.

4 Conclusion

To produce an effective CO_2 adsorbent the effects of different functionalisation methods on the properties of silica aerogels were investigated. Two methods for functionalisation of aerogels with amines were compared: co-condensation and post treatment. Both methods lead to the decrease of the surface area of the produced aerogels with increasing nitrogen content. The co-condensation allows the addition of up to 1.44 wt.% nitrogen into the aerogel. This nitrogen content results in a minor increase in adsorption capacity at low partial pressure, making the co-condensation functionalisation unsuitable for the production of a CO_2 adsorbing material in this application. The adsorption capacity of post functionalised aerogels is significantly increased (one order of magnitude at low partial pressure) at high nitrogen contents, despite their considerably lower surface area. Nitrogen content of 5.2 wt.% inside the aerogel results in a CO_2 adsorption capacity of up to 0.523 $\text{mmol}_{CO_2}/\text{g}$ (250 Pa), which is comparable to the state of the art adsorbent Zeolite 13X. In combination with the low temperature needed for desorption the post functionalised aerogels are promising adsorbents for CO_2 adsorption at low partial pressure.

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