Aminofunctionalized Silica Aerogels for CO_2 and Ethanol Adsorption from Aircraft Cabin Air

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Abstract

Adsorbents used in closed-loop environmental control systems for future aircrafts should exhibit a high CO_2 adsorption capacity at low partial pressures, a high selectivity for adsorbing CO_2, the ability to adsorb volatile organic compounds (e.g., ethanol), a high porosity and an open pore structure.

In this work, the applicability of amino functionalized silica aerogels as an adsorbent for this application is investigated and compared to the commercial adsorbent zeolite 13X. The high surface area, open pore structure and high porosity of silica aerogels are promising starting characteristics for an adsorbent.

The results indicate that the CO_2 adsorption capacity can be increased by two orders-of-magnitude by amino functionalisation. The breakthrough CO_2 adsorption capacity is not reduced by the presence of ethanol, favouring their application in CO_2 removal units in closed loop environmental control systems.

1. Introduction

To regenerate the breathing air in closed inhabited environments like in submarines and space crafts, closed loop environmental control systems are necessary. These systems also have the potential to increase the fuel efficiency of future aircrafts, because the amount of air to be pressurized to cabin conditions can be reduced. Also the cabin air quality can be increased, due to the elevation of the moisture concentration in the cabin. The main part of closed loop environmental control systems is the CO_2 removal unit, removing the human emission of CO_2 and other substances from the recirculated air. An adsorption process promises to be effective in this application due to the low regeneration temperature and the absence of a liquid cycle in comparison to absorption processes. Nonetheless, adsorption processes highly depend on the used adsorbent, which should be tailor-made for the proposed application. In the case of an application in the CO_2 removal system in closed loop environmental control systems, the adsorbents should possess a high CO_2 adsorption capacity at low partial pressure, be able to remove volatile organic compounds, be resistant to moisture, as well as possess a high porosity and an open pore structure (Wörmeyer et al., 2011).

The high surface area, open pore structure and high porosity of silica aerogels are promising starting characteristics for an adsorbent. The CO_2 adsorption capacity of the unmodified aerogels at low partial pressure is not sufficient for an application in a CO_2 removal unit,

bringing about the need for a functionalisation of the aerogels. Aminosilanes were selected for the purpose of functionalisation due the established knowledge of CO_2 amine interaction. The amines are introduced into the gel structure during gelation (co-condensation (cc)) or after gelation (post functionalisation) by surface modification of the gel. The produced gels are supercritical dried afterwards to produce an aerogel and subsequently characterised.
In this work, the utilization of amino functionalized silica aerogels as an adsorbent for this application is investigated and compared to the commercial adsorbent zeolite 13X.

2. Materials and Methods

2.1. Reagents

All materials used in this work are commercially available. The suppliers are Sigma Aldrich for the Zeolite 13X, Fluka for the tetramethylorthosilicate (TMOS) (98%), aminopropyltrimethoxysilane (APTMS) (97%) and Ethanol (99%). Methanol (99.5%), HCl (30%) and ammonia hydroxide (25%) were supplied by Merck. The (3-(Trimethoxysilylpropyl)-diethylenetriamine (AAAPTMS) (95%) was supplied by ABCR.

2.2. Processing

The aerogels in this work were produced by a two step method reported by Tillotson and Hrubesh (1992). The functionalisation was conducted according to the modification of Alnaief and Smirnova (2010) to the two step method.
The first step for the production of post functionalised aerogels consists in the mixing of: 1 mol TMOS: 2.4 mol methanol: 1.3 mol water: 10^{-5} mol hydrochloric acid to produce the sol, which was stirred at room temperature for 30 minutes. Ethanol was added in the second step to produce the desired density and additional water and ammonia solution were added to produce a gel. The final molar ratio was: 1 mol TMOS: 2.4 mol methanol: 4 mol water: 10^{-5} mol hydrochloric acid: 10^{-2} mol ammonia. The produced gels were aged for 48 h in ethanol. Afterwards, the produced gels were functionalised in an ethanol / APTMS solution two times the volume of the gel and stored for 48 h at 50°C. Prior to the supercritical drying with CO_2 the functionalised gels were washed with ethanol. The post functionalisation was also performed with AAAPTMS instead of APTMS.
For the cocondensation (cc)-functionalisation method, ammonia hydroxide was replaced by a varying amount of APTMS to catalyse the gelation. The solutions for the first and second step were prepared separately and cooled to 273 K before merging. The first step consists in the mixing of: (1-x) mol TMOS: 2.4 mol methanol: 1.3 mol water: 10^{-5} mol hydrochloric acid. Again the sol was stirred at room temperature for 30 minutes. The second solution consisted of ethanol and additional water and APTMS 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 mixed in cylindrical flasks with the solution of step 1 to produce a gel. The cylindrical gels produced in this way were then supercritically dried with CO_2 after 48 h of aging in ethanol.

2.3. Characterization

The isotherm measurements are performed by a Nova 3200e by N_2 adsorption (77K) as well as CO_2 adsorption (273K) in a pressure range of 0.002 – 1 bar. Additionally, a selected adsorbent showing high adsorption capacities in pure CO_2 is characterized by breakthrough curve measurements of CO_2 (2500ppm) and ethanol (10ppm) from air/CO_2/ethanol mixtures

supplied by Westfalengas. The flow rate of the gas was 1 l/min. This analysis is performed in a laboratory scale adsorption plant at 20°C at a pressure of 1 bar and the dimensions of the adsorber were 0.3 m length and a volume of 150 ml. Ethanol concentrations from 5 – 600 ppm can be detected from CO_2 / air mixtures by a Dräger Alcotest 6810 and the CO_2 concentration is measured by a Sick/Maihak S710 FINOR ND-IR extractive gas analyser. CHN analysis was performed with a Carlo Erba EA 1108 Elemental analyzer.

3. Results & Discussion

The produced aerogels were analysed for the application as CO_2 adsorbents in closed loop environmental control systems. Favourable for this application is a high CO_2 adsorption capacity at 2500ppm (250Pa in pure CO_2) and the breakthrough adsorption capacity should not be influenced by small amounts (10ppm) of volatile organic compounds. Because the volatile organic compound with the highest concentration in aircraft cabin air is ethanol (Dechow et al., 1997), this component was selected as reference component.
To produce silica aerogels with a high CO_2 adsorption capacity two different functionalisation methods were applied, due to the low CO_2 adsorption capacity of unmodified silica aerogel as shown in Figure 1. It is possible to produce aerogels with an increased CO_2 adsorption capacity with the post functionalisation method (Figure 1). In comparison to the commercially available zeolite 13X, the APTMS-post functionalised aerogel exhibits a comparable CO_2 adsorption capacity at low partial pressure. The CO_2 adsorption capacity of the AAAPTMS postfunctionalised aerogel is higher than that of the zeolite 13X at low partial pressure. This makes the post functionalised aerogels a favourable adsorbent material and justifies a closer look on the effects of the functionalisation on the aerogel structure.

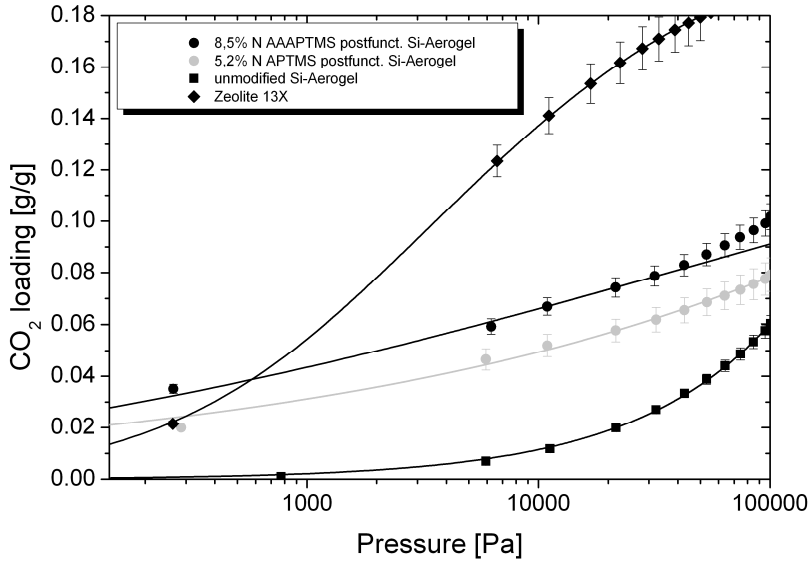

Figure 1: CO_2 adsorption isotherms of the post functionalised aerogels, unmodified silica aerogel and the Zeolite 13X

3.1 Influence of the nitrogen content on the surface area

In this section the influence of the degree of functionalisation on the surface area of the aerogels is presented. The degree of functionalisation is defined as the amount of nitrogen introduced into the aerogel structure, since the amino group is the only source of nitrogen in the production of aerogels. CO_2 adsorption is influenced not only by the content of the amine groups but may also be influenced by the surface area of the aerogel itself. Figure 2 shows the general trend of decreasing surface area with increasing nitrogen content for both functionalisation methods. Non-functionalised silica aerogels exhibit a surface area of 1000 m^2/g, a value that is not reached by the functionalised aerogels. For the co-condensation (cc)

functionalised aerogels the trend of decreasing surface area with increasing nitrogen content may be caused by the fast gelation and incomplete formation of the silica network. For cc functionalised aerogels Hüsing et al. (1999) also reports 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%.

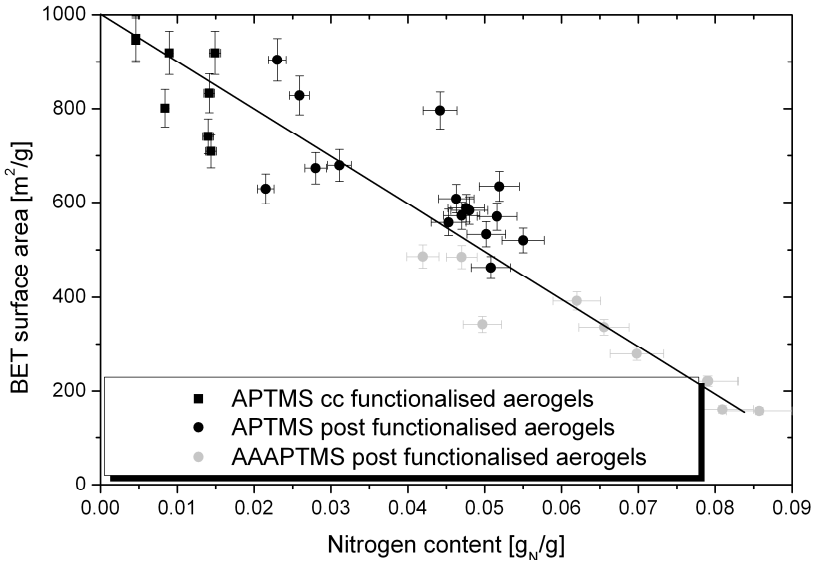

Figure 2: Surface area of the produced aerogels versus their nitrogen content.

The decrease in surface area at increasing nitrogen concentrations for the post functionalisation as shown in Figure 2 is also reported by Clavier et al. (2005) and Alnaief and Smirnova (2010). The trend may be induced by pore blocking of the grafted APTMS molecules. The nitrogen content of the post functionalised aerogels is much higher compared to the cc functionalised ones. The influence of the degree of functionalisation on the primary target of the functionalisation, the CO_2 adsorption capacity at low partial pressure, will be described in the following section.

3.2 Influence of nitrogen content on the CO_2 loading

The CO_2 loading at low pressures (250 Pa) is an important factor for the application of the functionalised aerogels in CO_2 removal units in closed loop environmental control systems. Therefore the effect of the nitrogen content of the produced aerogels on the CO_2 adsorption at 250 Pa is presented in Figure 3. The CO_2 loading increases with an increasing nitrogen content for both functionalisation methods. The cc-functionalised aerogels containing small proportions of nitrogen exhibit a low CO_2 loading despite possessing a high surface area, as shown in Figure 2. Due to this fact, cc functionalised aerogels are not suitable for their application as a CO_2 adsorbent. The APTMS post functionalised samples contain a higher amount of nitrogen and therefore show an increase in CO_2 adsorption capacity, while the AAAPTMS functionalised aerogels exhibit a higher nitrogen content and CO_2 adsorption capacity compared to the APTMS functionalised ones. These results indicate that the post functionalisation method is suitable for producing a promising material for an application as CO_2 adsorbents in closed loop environmental control systems.

Comparing these results to adsorption measurements by Franchi et al. (2005) and Harlick and Sayari (2006) at 5000 Pa CO_2 partial pressure in nitrogen with di- and tri-amine post

functionalised MCM 41 silica gels, the trend of increasing CO_2 adsorption capacity with increasing nitrogen content is expectable.

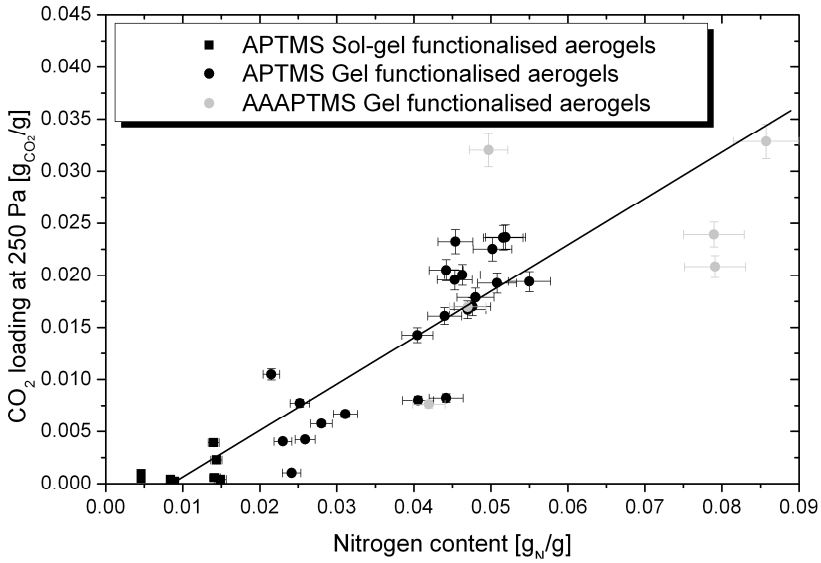

Figure 3: CO_2 loading at 250 Pa in relation to the nitrogen content of the functionalised aerogels

3.3 Influence of ethanol on the breakthrough loading of post functionalised aerogels

The proposed adsorbent material should not only possess a high CO_2 adsorption capacity at low partial pressure, but the breakthrough CO_2 adsorption capacity should also not be affected by small amounts of ethanol. Hence, in this section the breakthrough through post functionalised aerogel particles ($d_{p,s}$=0.0027 m) with a nitrogen content of 5.4 wt% and a surface area of 260 m^2/g is discussed.

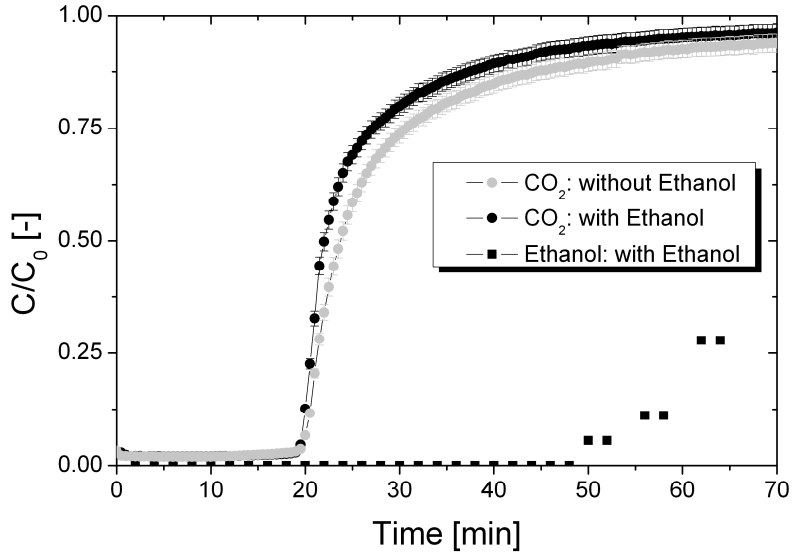

Figure 4: breakthrough of CO_2 and ethanol through APTMS functionalised aerogels with a nitrogen content of 5 wt%.

Figure 4 shows that the breakthrough time of CO_2 through aerogels is not changed by small concentrations of ethanol (10ppm). The breakthrough loading of the post functionalised aerogels is 0.009 g_{CO2}/g despite the presence or absence of ethanol. On the other hand, the saturation loading is affected by small concentrations of ethanol, resulting in 0.0113 g_{CO2}/g in the presence of ethanol compared to 0.0133 g_{CO2}/g in the absence of ethanol. Figure 4 also shows that the ethanol breakthrough appears much later compared to the breakthrough of

CO_2. Since the adsorber would be loaded until the appearance of the breakthrough of CO_2 in technical processes, the ethanol can be completely separated from the gas stream. Therefore an accumulation of ethanol in the recicurlated air is unlikely. In combination with the constant breakthrough CO_2 adsorption capacity, the ability to remove CO_2 and ethanol show the potential of the post functionalised aerogels for an application as CO_2 adsorbents in closed loop environmental control systems.

4. Conclusion

In order to produce an aerogel with favorable properties for an application as CO_2 adsorbent in closed loop environmental control systems, two functionalisation methods and two functionalisation agents were investigated. The results show that the CO_2 adsorption capacity can be increased by two orders-of-magnitude by amine functionalisation with APTMS and AAAPTMS post functionalized aerogels. The second method, being the co-condensation functionalisation, produced an aerogel with a minor increase in CO_2 adsorption capacity, which is not suitable as an adsorbent. Both functionalisation methods resulted in a decrease in surface area with increasing nitrogen content. The increased nitrogen content resulted in an increased CO_2 adsorption capacity at low partial pressures. The produced aerogels exhibit a high CO_2 adsorption capacity (3% (w/w) at 250 Pa, 0°C), outperforming the reference material zeolite 13X (2.1% (w/w)). The aerogels are also able to co-adsorb ethanol from CO_2 / ethanol / air mixtures, while the CO_2 breakthrough adsorption capacity is not reduced. The post functionalized aerogels promise to be effective adsorbents for the application in closed loop environmental control systems.

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