Adsorption of carbon dioxide adsorption on mesoporous porous silica materials containing amine-like motifs

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Introduction

CO_2 is separated from gas mixtures in various industrial applications, e.g. in enhanced oil recovery[1], natural gas processing, and in specialized CO_2 production plants. In the context of carbon capture, three different capture tactics are discussed and studied: post combustion, pre combustion, and oxyfuel or chemical looping capture. Different separation may be employed depending on the thermodynamic properties of the mixtures, the size of the CO_2 point source, and economical factors. In post combustion carbon capture, rather low partial pressures of CO_2 in a N_2 stream, alkanolamines are used in aqueous solutions. This use is because of their high reactivity, ease of reuse, and low absorption of hydrocarbons.[2] There are many disadvantages with this method, high energy consumption, severe corrosion of amine aqueous solution, and the re-pollution of the gas stream with water and amine vapor. This has limited its applicability from both an environmental and separation efficiency point of view.[3] More advanced solvents (ionic liquids), membrane technology and adsorption mediated separation have been proposed for low cost CO_2 separation. Porous adsorbents, with a comparably low heat capacity, high surface area and high stability, have been developed in industrial settings for similar gas separation applications.[4] CO_2 has a large electric quadrupole moment and physisorb easily to most surfaces. Porous materials have show large potential for CO_2 separation. Microporous materials may have a high selectivity for gas separation [5]; however, their small pores may slow down the cycle times in swing adsorption process. In this study we focused on the study of modifications of mesoporous (pore sizes 2-50 nm) materials, including their chemical modification and capacity for CO_2 uptake. These chemical modifications could enhance carbon dioxide separation efficiency with an easy regeneration of the adsorbents.

Functional mesoporous silica materials can be synthesized in different ways and we employ post-synthetically modifications of the materials with organo-silica groups[6]. This method is appealing for screening of different groups and other synthetic variables. To our knowledge, no studies have been published for silica materials modified with alkanolamine or amidine groups. Amidine molecules are reported to bind CO_2 readily at low CO_2 pressure in liquid solutions, and the chemical reaction is reversible at temperatures around 65 ºC.[7] We explored the potential for CO_2 separation in hybrid material, with amidine groups on a solid support. Silica materials with primary amine modification have been reported to enhance CO_2 adsorption.[8] In this study, we extended those by careful optimizing the conditions for the chemical reactions, and by comparing the capacity for carbon dioxide adsorption for these "amine-like" modifications.

The adsorption capacity (n) of CO_2 (dry and wet), and N_2 (dry and wet), on the organically modified mesoporous silica materials are characterized as a function of pressure (p) and temperature (T) conditions using a slightly modified commercial volumetric adsorption apparatus. The thermodynamic (*npT*) behavior for the solid-gas system is analyzed and compared for the samples with amine, alkanolamine or amidine moities. A certain propyl amine modified sample showed significantly large carbon dioxide adsorption capacity than the others. The propyl amine modified samples showed, consistently, a higher carbon dioxide adsorption capacity. In addition, a high selectivity of carbon dioxide adsorption was shown for the primary amines on a mesoporous solid support.

2. Materials and Methods

In this study, Davisil^{TM} (LC60A pore size 40-63 nm), was used as substrate for the post-synthesis "grafting" reactions. Thee chemicals were used as received from Aldrich. Gases (helium, carbon dioxide and nitrogen) were supplied by the Linde gas company. The modification of Davisil™ with aminopropyl groups was carried out according reported procedures and further optimized using the principles of factorial design. A series of final materials with a surface coverage of aminopropyl groups ranging from 1.56 to 4.16 groups/ nm^2 was obtained. The loading of organics were estimated from thermogravimetric analysis (TGA). The material with propyl bis(2-hydroxyethyl)amine was post-synthesized using similar procedure. The product with pending propyl N,N-dimethylacetamidine moieties, was prepared from the Davisil™ with aminopropyl groups. In this synthesis we employed the Scoggins' procedure for acetamidines.[9] A range of characterization methods (such as thermogravimetric analysis, nitrogen adsorption-desorption isotherms BET analysis, solid-state NMR spectroscopy) were used to study the composition and micro-structure of the materials.

The CO_2 and N_2 uptake capacity of the derived materials were studied under various thermodynamic conditions using a slightly modified Micromeritics Gemini^{TM} 2375 device (schematically shown in Figure 1). Before the experimentation, each sample was pretreated or regenerated under a flow of dry N_2 gas at a temperature of 140 °C for an extended amount of time. Humid gas (containing around 1.9% water) was produced to examine the effect of moisture on the adsorption capacity of carbon dioxide and nitrogen. Dry gas components (nitrogen or carbon dioxide, the partial pressure kept at 1.5bar) were bubbled through liquid water (kept in a temperature controlled room (23°C)). The temperature for the adsorption uptake experiment was controlled by a circulating bath (Huber ministat 230) and a Dewar (siloxane oligomer as heat transfer medium).

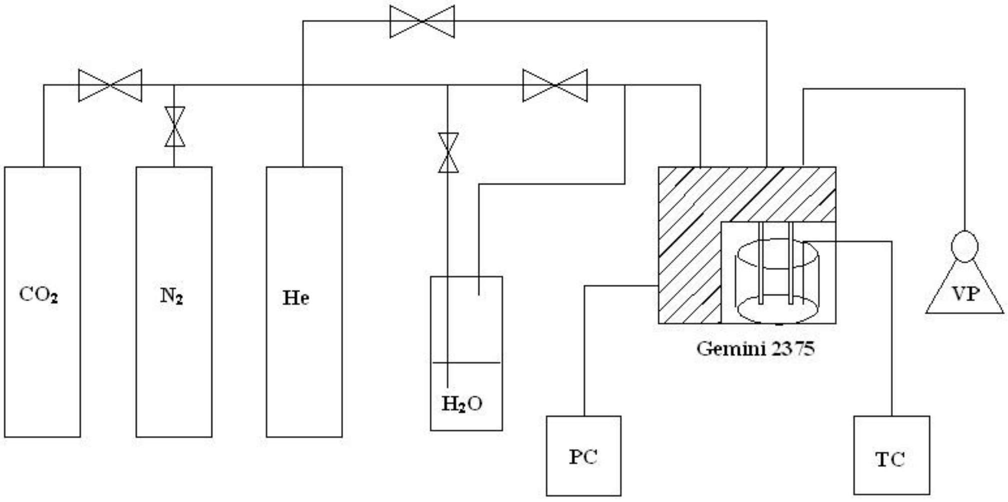

Figure 1: A representation of the volumetric adsorption device used to measure temperature and pressure dependent gas uptake. CO_2, N_2, and He denote gas bottles with pressure regulators. H_2O is liquid water, and Gemini 2375 a slight modified Micrometrics Gemini 2375 device. PC, TC, and VP, means pressure controller, temperature controller and vacuum pump.

3. Results and Discussions

3.1 Material synthesis

We have two major aims in modifying the mesoporous (2 – 50 nm) silica materials. One aim is to increase the degree of surface modification using multi parameter optimization. For this we employed Experiment of Design (the details of that optimization will be presented elsewhere). A second aim is to compare the binding efficiency for CO_2 adsorption and try to relate that to the density of organic fragments. Three amine-like moieties were chosen. The propyl amine modification have been studied by other researchers and a significant carbon dioxide uptake have been found[6,7,8]. Therefore we employed the multi parameter modification for this group. The other two surface modifications, propyl N,N-dimethylacetamidine and propyl bis(2-hydroxyethyl)amine, are new to our knowledge. In the liquid state these latter moieties have significant and interesting interactions with carbon dioxide.[1, 9]

The amount of organic material in the different materials was established by TGA. We are well aware about the potential for systematic errors associate with this methodology. In Table 1 the degree of modification is presented with the under the label loading. We achieved a surface coverage of 2.4 – 4.2 molecular amine fragments per nanometer squared. These values are comparable, if not higher, than those presented by others. [7]

Table 1. Presented are the surface areas, pore volumes, loadings and carbon dioxide uptake for modified mesoporous silica materials. The five last rows in the table refer to various propyl amine materials. The acetamidine sample is synthesized from the sample msf12.

Chemical Modification	**S_{BET} (m^2/g)**	**Pore size (nm)**	**Pore volume (cm^3/g)**	**Loading ($1/nm^2$)**	**CO_2 adsorption efficiency ($mmol/g_{ads}$)**		**N(efficiency) ***	
					No H_2O		No H_2O	
Unmodified Davsil™	540	63	0.87					
Propyl amine (Amd16)	199	67	0.33	4.16	1.40	2.13	0.45	0.69
bis(2-hydroxyethyl)-amino propyl	284	55	0.39	2.38	0.33	0.35	0.20	
N,N-dimethyl-	309	84	0.65	3.45	0.28		0.10	

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[*] The number N(efficiency) relates to a hypothesized case where the carbon dioxide adsorption is presumed to occur only on the amine moieties.

acetamidine propyl								
Amd7	284	62	0.44	3.55	1.34		0.49	
Amd13	361	62	0.56	2.49	0.89		0.44	
DTAS107	394	57	0.57	2.54	0.89	0.98	0.44	0.48
DTAS90	370	60	0.56	2.84	0.87	0.99	0.39	0.44
Msf12	347	75	0.65	2.70	1.25	0.90	0.56	0.40

All the samples were analyzed with nitrogen adsorption. As expected the BET surface decreased with an increased degree of modification. This effect is in particular visible for the various propyl amine modifications, presented in Table 1 as propyl amine (amd16), amd7, amd13, DTAS107, DTAS90, and Msf12. The amd16 modification has the smallest specific BET area and the highest loading of amine groups. For all the samples, the average pore size does not change significantly after modification but Msf12 and the sample with amidine, which were pretreated in boiling water for three hours.

The local arrangements of various molecular fragments were studied with solid-state NMR spectroscopy, under magic angle spinning conditions. The degree of condensation among the organosiloxanes was studied (for the aminopropyl modified samples) with solid-state ^{29}Si NMR spectroscopy, using direct and cross-polarization detection. The degree of condensation was found to be high. In addition it was realized (using solid-state ^{1}H and ^{13}C NMR spectroscopy) that the samples contained a small amount of non hydrolyzed ethoxy groups. The propyl N,N-dimethylacetamidine modification posed challenges to characterization; from TGA data and supported by NMR spectroscopy, we noted that only 30% of the amine functions where converted to the amidine functionality. On the other hand, it was concluded that the functionalization with both propyl amine and propyl bis(2-hydroxyethyl)amine was successful. In the next section, the carbon dioxide uptake on these samples are presented, besides for the less defined amidine sample.

3.2 Carbon dioxide uptake

The pressure dependency for the carbon dioxide uptake was measured under isothermal conditions (temperature between 0 – 70 °C, with or without water present). A volumetric adsorption device was used for this (Figure 1). Besides of being able to screen for an enhanced capacity for carbon dioxide uptake, these detailed measurements might inform about specific thermodynamic properties of the adsorbents. This combined pT information is important and interesting for swing adsorption, in particular for temperature swing adsorption (TSA) or thermally coupled PSA[5] mediated carbon dioxide gas separation.

The materials was screened by two factors: the gas (carbon dioxide, or carbon dioxide and water) uptake capacity per gram and the N(efficiency), according to the gas uptake at standard condition (25 °C and 1 atm). The uptake capacity of the propyl amine modified samples are significant, in particular the amd16 sample takes up significant amount of gas (see table 1). The uptake for the bis(2-hydroxyethyl)-amino propyl and N,N-dimethyl-acetamidine propyl modified samples were not promising and, hence, we did not optimize the synthetic conditions any further. The amount 1.4 mmol/ g corresponds to 6.2 wt% carbon dioxide and with “wet” carbon dioxide even more gas is adsorbed (2.1 mmol/ g). These values should be compared with some alternative microporous materials, which have capacities of 2-3 mmol/g at such standard pressures.[10]

In Figure 2 the carbon dioxide adsorption isotherms at 25 °C is presented. The propyl amine samples (amd16,13, 7; msf12; dats107, 90) all have higher uptake capacities than the bis(2-hydroxyethyl)amino propyl and a N,N-dimethylacetamidine propyl modified samples at all pressures.

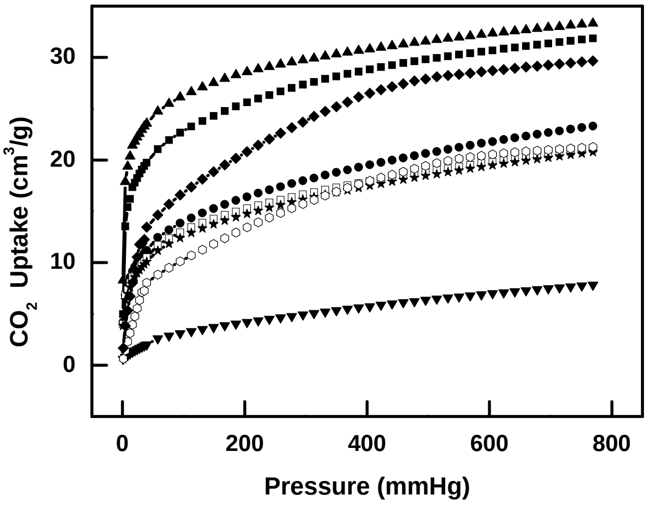

Figure 2. Carbon dioxide uptake on organically modified mesoporous silica materials, with different amine motifs at 25 ℃ without water present (propyl amine: ▲Amd16;■amd7;◆msf12;●dats107;□amd13;★dats90. amidine: ◇. bis-ethanol amine: ▼).

The carbon dioxide uptake in presence of water vapor was studied and is presented in Figure 3. For most samples the effect of water vapor is negligible. however the gas adsorption capacity of amd 16 is enhanced significantly with water present, which could be very well related to different degrees of hydrophobicity.

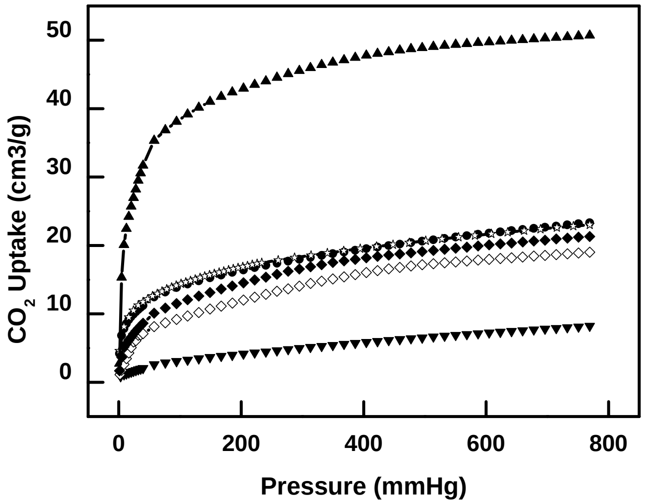

Figure 3. Gas uptake on organically modified mesoporous silica materials, with different amine motifs at 25 ℃ with water vapor present (propyl amine: ▲ Amd16;◆msf12;●dats107;☆ dats90. amidine: ◇. bis-ethanol amine: ▼).

The temperature dependent carbon dioxide adsorption isotherms for the bis(2-hydroxyethyl)amino propyl and propyl amine (amd16) sample are presented in Figure 4 and Figure 5. From these two sets of curves, clearly, the adsorption is much higher for the sample modified with propyl amine groups. The largest differences are in the low pressure regime, where the adsorption increases significantly in Figure 4. In a very simplified dual site

Langmuir model, the adsorption energies for the carbon dioxide on the propyl amine modified samples were estimated. This model did not describe the initial low pressure dependencies well; however, the dependencies at higher pressures ("the second step") is better described and corresponds to an adsorption energy of roughly 6 kcal/mol (10 kT) - a typical values for physisorption.

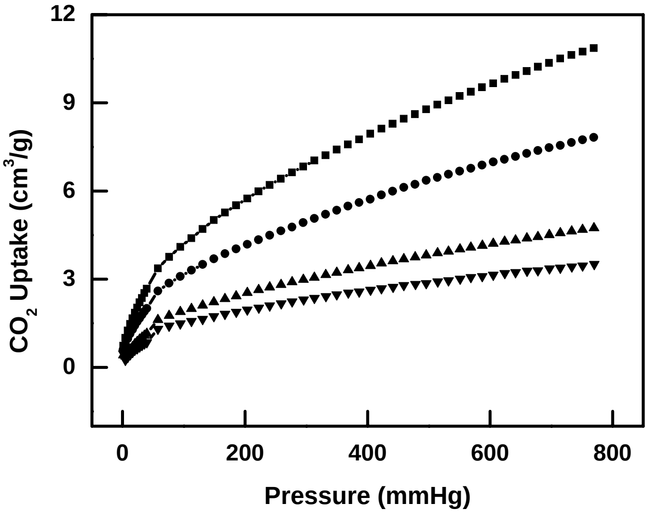

Figure 4. Carbon dioxide uptake in mesoporous silica materials modified with bis-ethanol amine groups at different temperature conditions, without water vapor present (■ 0℃;●25℃;▲50℃;▼70℃)

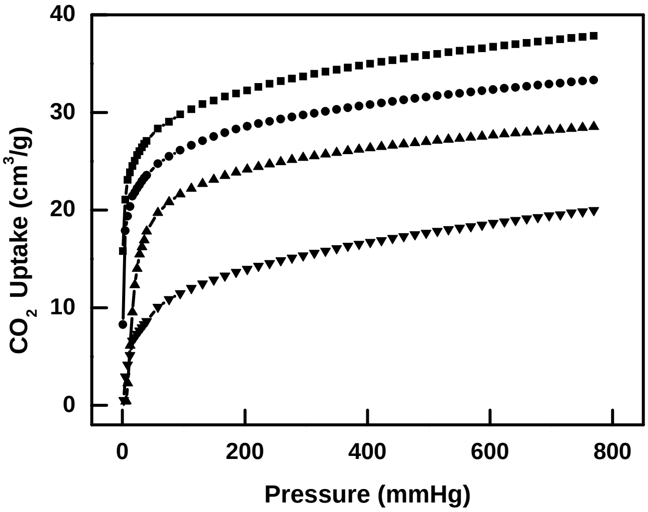

Figure 5. Temperature dependent carbon dioxide uptake capacity for propyl amine modified mesoporous silica materials (amd16) without water vapor present. (■ 0℃;●25℃;▲50℃;▼70℃)

The selectivity of carbon dioxide over nitrogen adsorption is very important for gas separation of flue gases. The propyl amine modified materials have significant selectivity. At a carbon dioxide pressures of 1 atmosphere the selectivity of CO_2 is between 30-50 depending on the temperature (at a higher temperature the selectivity is higher); at lower pressures, where both gases adsorb in a Henry's law manner, this selectivity is larger. The high selectivity for the amine modified materials is significantly higher than for zeolites or active carbons. Zeolites adsorbents show carbon dioxide selectivity of about 15 and active carbons of about 5-10 [ref] at an atmospheric pressure of either carbon dioxide or nitrogen gas.[16] It is not fully clear for us if the high selectivity is a reflection of a "chemisorption" nature on these amine modified materials.

4. Conclusions

A range of propyl amine modified mesoporous silica materials have been synthesized and studied. By careful optimization a specific loading of over 4 propyl amine per nm^2 was achieved. In addition, propyl bis(2-hydroxyethyl)amine and propyl N,N-dimethylacetamidine moieties were attached to mesoporous silica materials, for the first time.

The carbon dioxide uptake was significantly higher on propyl amine modified samples than on the amidine and bis-ethanol amine modified samples. The lower carbon dioxide uptake indicates that amidine and bis-ethanol modifications are less useful in adsorbents for carbon dioxide separation from flue gases.

On a silica adsorbent modified with propyl amine groups 1.4 mmol/ g carbon dioxide can be adsorbed at standard conditions of 25 ºC and 1 atmosphere. This value is similar to those for microporous materials (zeolites or metal organic frameworks) or active carbons. Speculatively, the larger pores enable faster molecular diffusion, which could allow for faster adsorption cycles. The carbon dioxide selectivity (over nitrogen) was determined to be comparably high on these materials. The high capacity, large pore size, and significant carbon dioxide selectivity, all combined indicates that these or similar materials are important candidates for carbon dioxide adsorbents.

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