AMINOPROPYL-FUNCTIONALISED SILICAS AS HIGH CAPACITY CO_2 ADSORBENTS

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Introduction

One approach to reduce greenhouse gas emissions from fossil fuel combustion and so maintain the future viability of coal fired power generation is to capture and then sequester the product CO_2. Thus, there is growing interest in the development of improved CO_2 capture and separation technologies. The development of high capacity, CO_2 selective adsorbents that can be used in pressure swing adsorption (PSA) processes is one way forward.

Adsorbents based on high surface area inorganic supports that incorporate basic organic groups, usually amines, are of particular interest. The interaction between the basic surface and acidic CO_2 molecules may result in the formation of surface ammonium carbamates (Figure 1)[1-3]. Thus, in dry CO_2, adsorption capacities are limited to 1 mole CO_2 for every 2 moles surface bound amine groups. Therefore it is desirable to develop adsorbents with the highest possible concentration of basic nitrogen groups accessible to CO_2.

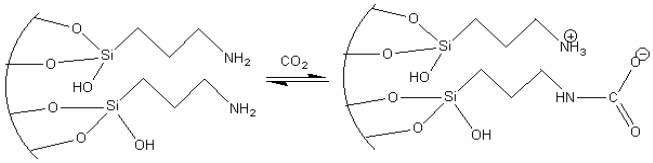

Figure 1. Surface reaction of tethered amine groups with CO_2.

A number of groups have now reported the preparation of 3-aminopropyl-functionalised silicas based on the derivatisation of mesoporous amorphous silica gels[3-7] and/or mesoporous periodic framework structures like SBA-15[2,5], MCM-41[1,8,9] and MCM-48[6]. Such mesoporous substrates are attractive because they possess pores that are (believed to be) large enough to access with derivatising reagents. Post-functionalization, they (are believed to) still retain sufficient porosity to facilitate rapid gas diffusion to and from the surface as required by the PSA process.

The specific CO_2 adsorption capacities reported for any of these materials to date are not outstanding. However, there is insufficient data in the literature to distinguish whether the limitation in CO_2 adsorption capacity is due to sub-optimal coverage of the mesopore surface with amine groups, due to poor accessibility of CO_2 to the surface amine groups, due to geometric constraints limiting the acid-base interaction at the surface and/or other unknown factors.

This report describes an investigation into the effects of mesopore structure (e.g., pore geometry, pore spacing, pore volume, surface area and surface silanol concentration) on the extent of surface functionalization and consequent CO_2 adsorption capacities. A new approach to characterizing the extent of surface modification (per unit of substrate surface area) is described and applied to the prepared materials, providing a better understanding of the modification and adsorption phenomena.

Experimental

Silica substrates. Amorphous silica gel 40 (Sigma Aldrich) was treated at 475 °C to give silica substrates S2 with a surface silanol concentration of 2.0 (i.e., 2 hydroxy groups per nm^2)[10].

Mesoporous periodic structures of the HMS type were prepared via a neutral templating technique using dodecylamine[11]. For HMS substrate H2, the template was removed by calcination at 475°C. By analogy with the work of van der Voort *et al*[10] this material is also estimated to possess 2 silanol groups per nm^2. For HMS substrates H5a, H5b and H5c, the template was removed via EtOH extraction. Following treatment at 150°C under vacuum, it is estimated that these substrates possess approximately 5 silanol groups per nm^2.

Substrates H2 and H5a-c all gave XRD peaks expected for HMS materials and indicated pore center separations of 46, 44, 32 and 38Å, respectively.

Preparation of aminopropyl-functionalised substrates. Approx. 1g of each pre-dried substrate was dispersed in 100 ml dry toluene and treated with variable quantities of aminopropyl-trimethoxysilane (apts), always in molar excess relative to the estimated silanol content of the substrate. Treatment proceeded at room temperature for 2 hours in most cases. The product was collected, washed with several volumes of dry toluene, then dried at 150°C for 24 hours under vacuum to complete the surface modification and also to remove residual solvent and silane.

Characterization of Materials. N_2 adsorption/desorption experiments were conducted at –196°C using a Micromeritics ASAP 2010 instrument. Total pore volumes were calculated from the N_2 volume adsorbed at P/P_0= 0.995. BET surface areas were determined from N_2 volume adsorbed over the partial pressure range 0.08 – 0.12. BJH pore diameters were determined from the N_2 volume desorbed between P/P_0 = 1 and P/P_0 = 0.15. Elemental analyses were determined by CMAS Pty Ltd, Belmont, Vic. for C and N. X-Ray diffraction (XRD) data were recorded using a Scintag X-Ray Diffractometer. For HMS materials, the distance between pore centers (s) was calculated from the distance between d_{100} symmetry planes (d) for the major diffraction peak between 1 and 5 (2θ) as follows: $s=2d*3^{0.5}$.

Carbon Dioxide Adsorption. CO_2 adsorption experiments were conducted on a Setaram Thermogravimetric Analyzer (TGA). Typically, samples were dried at 150 ºC, then cooled to 20ºC under a flow of dry Ar. The gas flow was then switched to a mixture containing 90% CO_2 and 10% Ar. Adsorption capacities were determined from the weight increase observed after 10 minutes.

Extent of Surface Modification (tether-loading). The extent of substrate modification by apts treatment was characterized as the number of tethers per nm^2 of <u>substrate</u> surface area ('tether-loading'). The tether-loading was calculated by assuming a cylindrical pore model based on the BJH pore radius (r_{prod}), the N content (N_{prod}) and the surface area (SA_{prod}) of the product, together with the BJH pore radius (r_{sub}) of the substrate, according to the following equation:

$$\frac{\#tethers}{SA_{sub}} = \frac{N_{prod}(g.g^{-1}) * \frac{6.023*10^{23}(atoms.mol^{-1})}{AtomicWt[N].(g.mol^{-1})}}{SA_{prod}(m^2.g^{-1}) * 10^{18}(nm^2.m^{-2})} * \frac{r_{prod}}{r_{sub}} * \frac{\#tethers}{\#N}$$

Results and Discussion

Table 1 provides basic preparation and characterization details for each of the substrate and product materials used in this study.

The results show that, in each case, treatment with apts led to reduction in pore volume, pore diameter and surface area and also led to an increase in both N and C content. The x-ray diffraction patterns for the HMS product materials were only slightly broadened relative to their corresponding substrates, demonstrating that the ordered framework structure was retained throughout modification.

The molar C/N ratios of the modified materials are consistent with the formation of tethers that (on average) are linked to the surface in either a tridentate fashion, or else in a bidentate fashion where the third methoxy group from apts has been hydrolysed (as illustrated in Figure 1) or crosslinked to an adjacent tether. However, given the density of silanol groups at the surface (2 to 5 per nm^2), tridentate coordination is considered unlikely.

It is noted that the H5c-p96 material has a higher N content (mass basis) than any other aminopropyl-functionalised silica material reported to date. Nevertheless, the H5c-p96 material has a

lower tether-loading than values reported for similar, but lower surface area substrates[4,7]. This suggests that it should be possible to prepare materials with still higher N content.

Table 1. Basic Preparation and Characterization Details for Substrate and Product Materials*

	Vol apts added $ml.g^{-1}$	SA $m^2.g^{-1}$	Pore Vol $ml.g^{-1}$	BJH dia. Å	N mass %	C mass %	CO_2 adsorb mass%
Typical Std Dev	± 0.1	± 10	±0.02	± 0.4	± <0.1	± <0.1	± 0.1
S2		567	0.67	36.8	-	0.0	1.57
S2-p2	1.25	419	0.45	36.3	1.6	4.3	2.74
H2		909	1.06	29.6	-	0.5	2.17
H2-p2	4.0	706	0.66	23.2	2.5	6.9	3.50
H5a		762	1.02	30.0	<0.1	3.2	2.18
H5a-p2	4.0	638	0.60	25.2	2.7	7.0	4.02
H5b		1268	-	24.1	<0.1	0.0	n/a
H5b-p2	3.0	1194	-	20.3	2.3	8.5	3.14
H5c		1198	-	20.6	-		2.66
H5c-p2	4.0	1176	-	20.4	2.1	6.4	3.80
H5c-p24	4.0	1125	-	19.0	3.2	9.4	6.31
H5c-p96	4.0	1113	-	19.5	3.4	9.3	5.70
H5c-p96r	4.0	1195	-	19.3	3.3	9.3	6.14

* p: product; 2/24/96: 2/24/96h treatment @ RT; 96r: 96h treatment @ reflux

Figure 2 illustrates the tether-loading of the various product materials as a function of the quantity of silane added to the reaction mixture per unit substrate surface area. As illustrated by the trend line, the results show that the higher quantities lead to improved tether-loadings (for 2h treatment of HMS substrates).

It can be noted that products from substrates with both low (2.0) and high (5.0) silanol content fall on this trend line, indicating that, within the range of preparative procedures investigated, higher silanol content does not necessarily lead to higher tether loadings.

The product prepared from amorphous silica, S2-p2, gave a substantially higher tether-loading than for the HMS derived products at low silane concentration. It is thought that the morphology of the amorphous silica, i.e., the greater accessibility of the mesopores and the larger average pore diameter, permits better entry and faster diffusion of reagent molecules.

Figure 2 also indicates that longer treatment times (H5c-p24) lead to improved tether-loadings for the HMS substrates, presumably because additional time helps to overcome diffusion limitations within the mesopores. However, extending the treatment beyond 24 hours (H5c-p96) or to higher temperature (H5c-p96r) does not lead to any further increase in tether-loading. Thus, it appears that for these conditions equilibrium loadings have been achieved.

It is interesting that the apparent equilibrium loadings for the HMS substrates are lower than for Silica 40 at the same apts concentration. The reason is unclear, but one possibility is that the sharper internal curvature of the HMS cylinders makes it more likely that initially adsorbed apts-tethers will block access of subsequent apts groups to the surface.

Table 1 also lists the CO_2 adsorption capacity determined for each material on a mass % basis. To our knowledge the capacity reported for H5c-p24 (6.31%) is the highest yet reported for any apts functionalised material[4,5,11,12]. All products exhibited capacities that correspond to a CO_2/N molar ratio of ~0.5, consistent with the postulated carbamate mechanism. Marginally greater CO_2/N ratios observed for products with lower tether-loadings are probably due to the occurrence of some additional CO_2 adsorption at surface silanol sites.

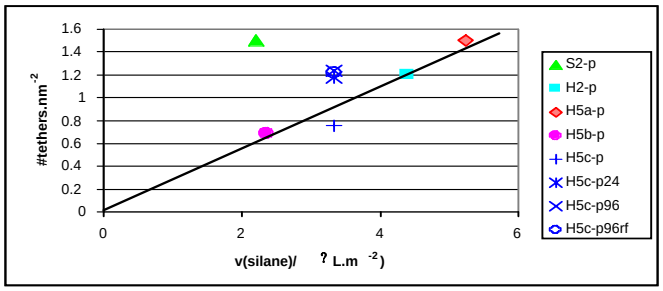

Figure 2. Tether-loading of aminopropyl-functionalised mesoporous

Figure 3 shows the CO_2 adsorption capacity of each material as a function of tether-loading. There is a general increase in capacity at higher loadings. However, the most significant observation is that the higher surface area substrates lead to apts modified products with the best CO_2 adsorption capacities (on a mass basis).

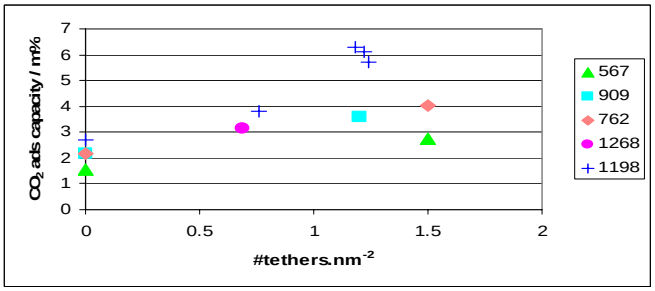

Figure 3. The CO_2 adsorption capacity of materials prepared from the various substrates as denoted by substrates surface area.

Conclusions

The characterization of these organic-inorganic hybrid adsorbents on the basis of substrate surface area has usefully enhanced our understanding of the factors which have, so far, limited the extent of surface functionalization and, consequently, the CO_2 adsorption capacities that can be achieved. In the course of this work, we have prepared hybrid adsorbents (of this type) with the highest N loadings and highest CO_2 adsorption capacities so far reported and expect to be able to improve upon this further.

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