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Adsorption of CO_2 on mesocellular siliceous foam iteratively functionalized with dendrimers

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Abstract Melamine-type dendrimers are grafted to mesocellular siliceous foam (MCF) with ultralarge mesopores by stepwise alternating treatments of the substrate with 2,4,6-trichlorotriazine and ethylenediamine. MCF grafted dendrimers up to 4th generation are prepared and characterized. Very high organic loadings (55 wt% at the 4th generation) are achieved, with half of the initial substrate mesopores volume remaining unoccupied—leaving room for the rapid ingress and egress of small gas molecules. The product materials possess relatively high thermal stability—their decomposition starts at around 300 °C. Adsorption measurements suggest that only the primary amine groups of these melamine type structures are active for CO_2 chemisorption. The CO_2 adsorption capacities of these adsorbents are improved relative to the unfunctionalized MCF, especially when considered on a wt% substrate basis.

Keywords Mesoporous material · Mesocellular siliceous foam · Melamine dendrimer · Functionalization · CO_2 adsorption

1 Introduction

Concern about global warming has intensified dialog across society to consider the potential technologies for large-scale carbon dioxide capture and sequestration (CCS) (Gough 2008). At their current level of development, CCS technologies are regarded to be insufficiently cost effective or energy efficient. This has triggered studies to improve existing technologies and generate new ones (Kosugi et al. 2004). Two of the most commonly considered approaches to capture CO_2 emissions from large point sources, such as coal fired power stations, are chemical absorption and physical adsorption.

Chemical absorption, by amine solvents (e.g. monoethanolamine, diethanolamine, methyldiethanolamine, and triethanolamine), has long been used in industry for acid gas removal (Kohl and Nielsen 1997). Chemisorption solvents possess high CO_2 selectivity due to chemical reaction between CO_2 and amines. However they possess some disadvantages, for example a high energy requirement for regeneration of the absorbents because of chemisorption, loss of effectiveness over time due to low thermal stability, loss due to evaporation and their tendency to induce corrosion. Physical adsorption by microporous activated carbon and zeolites, has been reported to provide high CO_2 adsorption capacity at ambient temperature. However, this capacity declines rapidly with increasing temperature. Besides that, the selectivity of these materials is low since adsorption is a physical interaction rather than a chemical one. Also CO_2 adsorption by zeolite in the presence of moisture is inhibited as the water-zeolite interaction is stronger, and high temperature regeneration is needed (Siriwardane et al. 2001).

Recently, hybrid organic-inorganic mesoporous materials have appeared as potential CO_2 adsorbents (Huang et al. 2003; Delaney et al. 2002; Knowles et al. 2005; Hiyoshi et al. 2004; Chang et al. 2003; Khatri et al. 2005; Zheng et al. 2005; Kim et al. 2005; Harlick and Sayari 2007; Xu et al. 2002). These materials can be synthesized in two ways: post-synthesis grafting and co-condensation (Stein et

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al. 2000; Hoffmann et al. 2006). The former method involves attachment of organic components onto preformed mesoporous substrates, while the latter method involves simultaneous condensation of inorganic (silica) and organic species using, for example, silane-coupling agents. Consequently the organic functional groups are placed on the pore surfaces (former method) or within the wall of mesoporous materials (latter method). Post-synthesis grafting pore surfaces of mesoporous silica substrates by aminosilanes (APTS) has resulted in high CO_2 adsorption capacities (11.7 wt%) at 25 °C and 1 atm for a dry 5% CO_2 in N_2 feed mixture (Harlick and Sayari 2007), while the capacity for the unmodified substrate at the same experimental condition was only around 2.0 wt% (Huang et al. 2003). Other advantages of these materials are high thermal stability relative to amine solvents, good water tolerance relative to zeolite and high selectivity towards CO_2 relative to both zeolite and activated carbon (Siriwardane et al. 2001). However, the CO_2 adsorption performance of these hybrid organic-inorganic mesoporous materials are still not sufficiently high due to the limited number of amine sites available to capture CO_2. Recently polyethylenimine (PEI), which contains a high concentration of amine groups, has been impregnated into mesoporous substrate MCM-41 (75 wt% PEI). This resulted in a significantly improved CO_2 adsorption capacity, e.g. 13.3 wt% at 75 °C (from a 100% CO_2 gas stream) as a result of the high amine loading (Xu et al. 2002). Thus the preparation of hybrid organic-inorganic mesoporous materials containing a high concentration of amine sites has resulted in the generation of more effective and efficient CO_2 adsorbents.

Dendrimers are highly branched macromolecules that radiate from a central core with a repeating motif of branching groups. The size, molecular weight, and chemical functionality of dendrimers can be easily controlled through divergent or convergent synthetic methods. There are now examples in the literature of where dendrimers have been grown from the surface of mesoporous substrates. For example, poly(amidoamine) (PAMAM) dendrimers up to the fourth generation have been grafted on the pore surfaces of pore-expanded (10.6 nm) MCM-41 (Reynhardt et al. 2004, 2005). 4-aminomethylpiperidine branched melamine-based dendrimers were also grown within mesopores of MCM-41 and SBA-15 by means of a stepwise alternating treatment of the substrate with 2,4,6-trichlorotriazine and 4-aminomethylpiperidine (Acosta et al. 2004). It was found that the growth of 4-aminomethylpiperidine branched melamine-based dendrimers within 4.2 nm pore diameter MCM-41 and 8.3 nm pore diameter SBA-15 was limited to two and four generations, respectively by virtue of the pore volume available. These studies concluded that the pore size of the mesoporous materials played an important role in dendrimer growth. Therefore the use of mesoporous materials with larger pore size is a potentially promising approach if higher generation dendrimer could be incorporated.

Mesocellular siliceous foams (MCF) consist of uniform spherical cells in the diameter range of 16-42 nm that are interconnected by uniform windows to create a continuous 3D pore system (Schmidt-Winkel et al. 1999, 2000). MCF possess the largest pore size among all the mesoporous materials discovered during the last decade. They have been utilized as supports for protein separations and enzyme immobilization because of their ultralarge pore size and high loading capacity compared to other mesoporous materials, such as MCM-41, MCM-48, and SBA-15 (Han et al. 2002). Therefore MCF could be a good substrate for the incorporation of larger molecules, such as dendrimers and which might facilitate higher loadings.

This study reports the preparation and characterization of a series of MCF bound melamine-based dendrimers by means of a stepwise alternating treatment of the substrate with 2,4,6-trichlorotriazine and ethylenediamine, together with their CO_2 adsorption properties. Ethylenediamine branched melamine-based dendrimers contain a mixture of primary, secondary and tertiary amines groups. Thus, they are interesting from the perspective that they provide a range of active sites with varied basic strength, rather than a single fixed value. In addition it provides a method for direct adjustment of the surface bound amine concentration per constant unit of pore volume of the substrate.

2 Experimental

2.1 Chemicals

Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer non-ionic surfactant $EO_{20}PO_{70}$-EO_{20} (Pluronic P123) was provided by BASF. Tetraethyl orthosilicate (TEOS 98%), 1,3,5-trimethylbenzene (TMB), hydrochloric acid (HCl), ethanol (EtOH), NH_4F, 3-aminopropyltrimethoxysilane (APTS), toluene, cyanuric chloride, diisopropylethylamine and ethylenediamine were purchased from Aldrich.

2.2 Preparation of adsorbents

2.2.1 Preparation of MCF and propylamine-functionalized MCF

The MCF was prepared in aqueous hydrochloric acid using dilute solutions of the nonionic block copolymer surfactant Pluronic P123 with TMB as the organic swelling agent following the literature (Schmidt-Winkel et al. 1999, 2000). Briefly, P123 (8.0 g) was dissolved in 1.6 M HCl (300 ml) at room temperature while being stirred in a beaker covered with a watch glass. TMB (9.3 ml) and NH_4F (92 mg) were then added, and the mixture heated to 37–40 °C. Following

60 min of stirring, TEOS (19.2 ml) was added. After 20 h stirring at 37–40 °C, the milky reaction mixture was transferred to an autoclave and aged at 100 °C for 24 h under static conditions. The mixture was then cooled down to room temperature, and the white precipitate was isolated by filtration, dried in air for at least 2 days, and calcined at 500 °C for 8 h in air to produce the MCF materials. Propylamine-functionalized MCF was prepared as follow (McKittrick and Jones 2003): The MCF was dried in vacuum oven for 24 h at approximately 50 °C. Then it (∼5 g) was placed in a 500 ml round bottom flask that contained toluene (350 ml) and a drying tube filled with $CaCl_2$. To this mixture 3-aminopropyltrimethoxysilane (APTS) (7.1 ml, 30.5 mmol) was added. Then the reaction was stirred for 44 h at RT. The solid was then collected by filtration and washed three times with 50 ml toluene. This solid is referred to in this paper as MCF/G0.

2.2.2 *Functionalization of MCF by melamine-based dendrimers*

MCF/G0 functionalized by melamine-based dendrimers were prepared by using a method similar to that reported in the literature (see Scheme 1) (Acosta et al. 2004). Cyanuric chloride (5.5 g, 30 mmol) and diisopropylethylamine (7.8 ml) were dissolved in THF (100 ml) in a round bottom flask. This mixture was stirred at 0 °C. MCF/G0 (∼4 g MCF) was added with continuous stirring to the above mixture. After that the mixture was left to react at 0 °C for 24 h. Afterwards the solid was filtered and washed twice with methanol (40 ml), dichloromethane (40 ml) and THF (40 ml). The washed solid was then collected and added to a mixture of ethylenediamine (3.9 ml, 72 mmol) that was dissolved in THF (100 ml). The mixture was refluxed for 24 h at 65–70 °C. The solid was collected by filtration then washed as previous described. This solid is referred to as MCF/G1. Repeating the preceding procedure led to products MCF/G2, 3 and 4.

2.3 Characterization of adsorbents

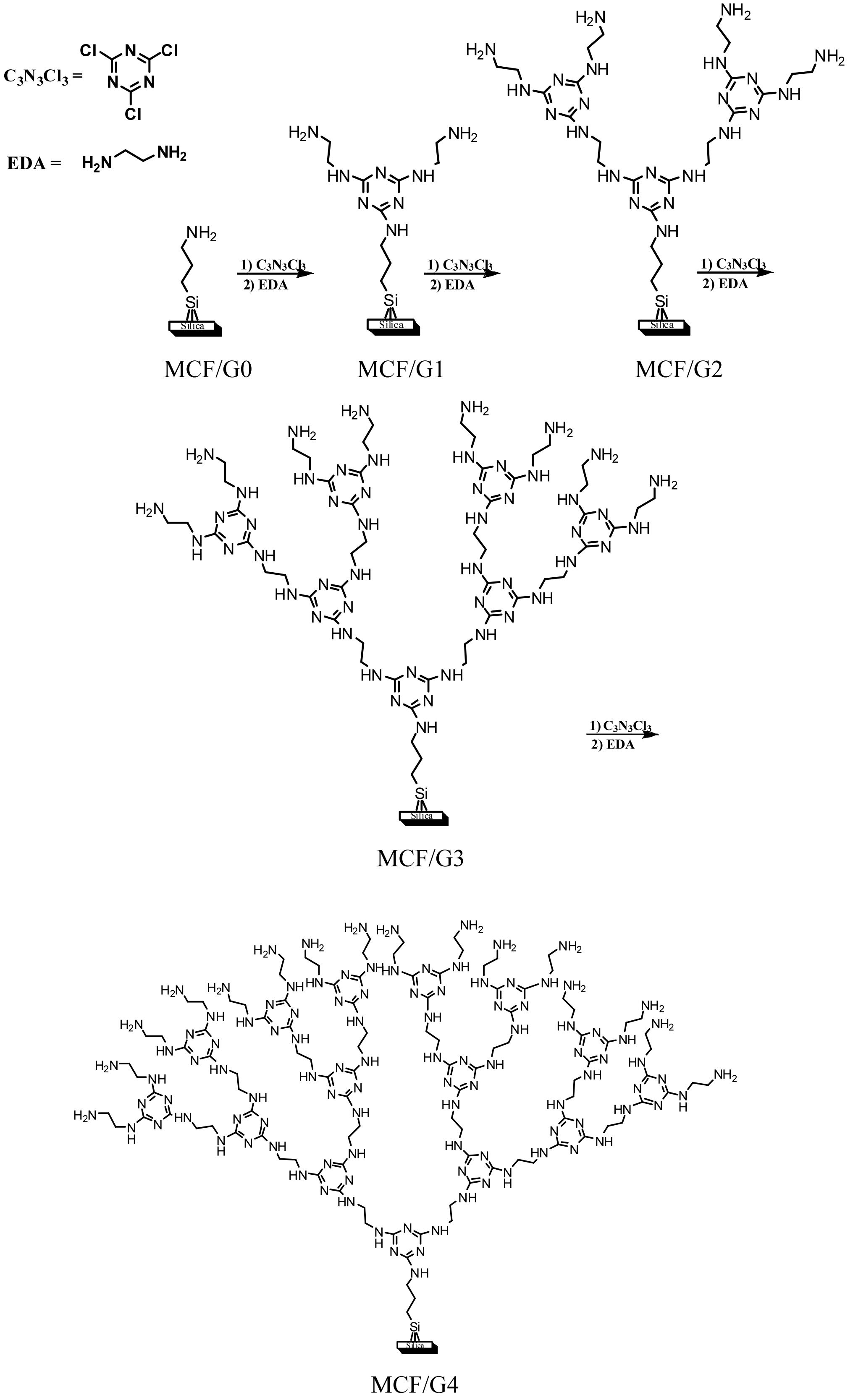
Fourier transform infrared spectra (FTIR) were collected on a BIO-RAD FTS 40 spectrometer using KBr pellets at room temperature. The MCF materials before and after progressive dendrimer functionalization, were characterized by N_2 adsorption/desorption. The N_2 adsorption/desorption isotherms were obtained at 77 K on a Coulter CX-300 adsorption apparatus. Each sample was outgassed at 105 °C for 24 h using a high vacuum line prior to nitrogen adsorption. Surface area and total pore volume were determined using the BET equation and the BJH method, respectively. The pore size was calculated from analysis of the adsorption branch of the nitrogen isotherm. The window size was calculated from analysis of the desorption branch of the nitrogen isotherm. Thermogravimetric analysis (TGA) of MCF/melamine-based dendrimers was also carried out using a PerkinElmer Analyzer. About 5 mg of the sample was heated from room temperature to 150 °C at 10 °C/min in nitrogen, held for 90 min at 150 °C in nitrogen, heated from 150 °C to 650 or 800 °C at 10 °C/min in air. Elemental analyses (C, H and N) were carried out by Campbell Microanalytical Laboratory, University of Otago, New Zealand.

2.4 CO_2 adsorption/desorption measurement

Carbon dioxide adsorption/desorption was measured by combined TGA and differential thermal analysis (DTA) using a Setaram Thermogravimetric Analyzer (Knowles et al. 2005). The weight change of the adsorbent was followed to determine the adsorption and the desorption performance of the materials. Prior to a CO_2 adsorption/desorption experiments, the previously adsorbed moisture and CO_2 were removed as follows: about 10 mg of the adsorbent was placed in a small sample cell, heated to 105 °C in flowing Ar (70 ml/min), and held at 105 °C until its weight became constant (about 90 min). The temperature was then adjusted to 20 °C for the CO_2 adsorption/desorption measurements. In a typical adsorption/desorption process, 90% CO_2/10% Ar mixture adsorbate was introduced at a flow rate of 70 ml/min for 10 min. After adsorption of CO_2, the gas was switched to 99.995% pure Ar at a flow rate of 70 ml/min for another 10 min to perform the desorption. The CO_2 adsorption capacity and heat of adsorption were calculated from the DTA/TGA data.

3 Results and discussion

The FTIR spectra of these functionalized materials (MCF/G0, 1, 2, 3 and 4) and the unfunctionalized material (MCF) are shown in Fig. 1. A broad absorption band at 3450 cm^{-1} on the unmodified MCF is attributed to the O–H stretching vibrations of silanol groups and water molecules adsorbed. The band at 1630 cm^{-1} is attributed to adsorbed water. The broad absorption band has been weakened considerably after modification with APTS, indicating hydroxyl groups reacted with APTS. The IR bands at 3422 and 3277 cm^{-1} are due to the asymmetric and symmetric NH_2 stretchings (Huang et al. 2003; Khatri et al. 2005). The IR bands at 2979 and 2938 cm^{-1} are attributed to the CH stretching in propyl chain. The bands at 1636, 1540, 1473 cm^{-1} are attributed to the formation of aminobicarbonate salt species due to CO_2 adsorbing on the aminopropyl modified MCF (Chang et al. 2003).



Scheme 1 Illustration of the stepwise synthesis of melamine-based dendrimers on MCF

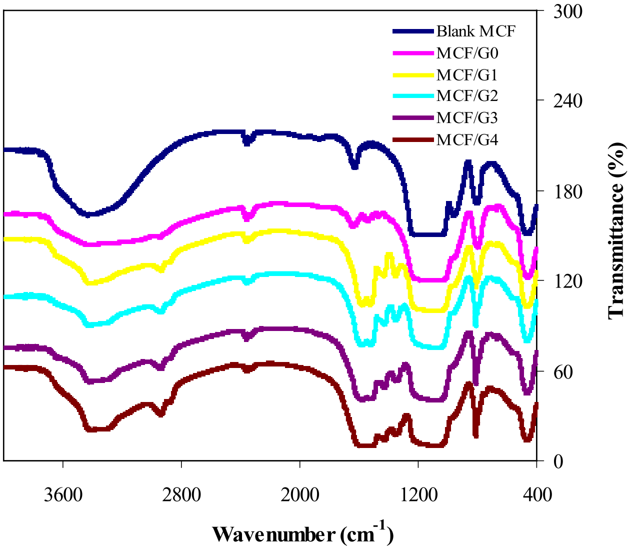


Fig. 1 FTIR spectra of MCF and its functionalized products. The transmittances (%) are shifted upwards by 150, 120, 100, 75, 40 and 10 for MCF, MCF/G0, 1, 2, 3 and 4, respectively

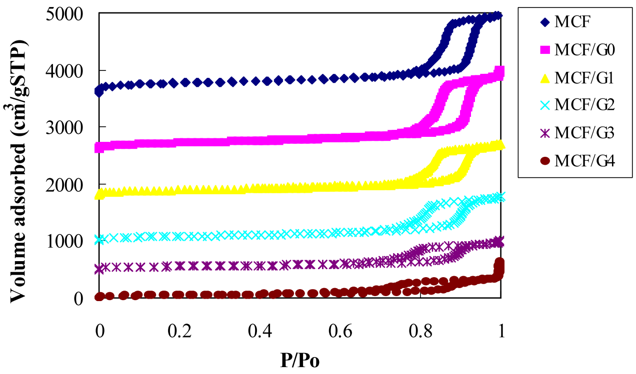


Fig. 2 Nitrogen adsorption/desorption isotherms for MCF and its functionalized products. The volumes adsorbed (V) are shifted upwards by 3600, 2600, 1800, 1000 and 500 cm^3/g-STP for MCF, MCF/G0, 1, 2 and 3, respectively

The spectra of MCF/G1-4 reveal new bands at ~1582 and ~1524 cm^{-1}, which are attributed to the C=N stretching in the triazine ring, indicating the growth of melamine based dendrimers. The N–H stretches can be observed at 3200–3500 cm^{-1}. The N–H absorption band at ~1600 cm^{-1} range was not observed due to overlapping with strong C=N absorption bands. The intensities of IR bands of C=N (~1582 and ~1524 cm^{-1}) and CH$_2$ (2938 and 2892 cm^{-1}) increased with increasing dendrimer generation, indicating the growth of dendrimers.

Nitrogen sorption isotherms of these functionalized materials (MCF/G0, 1, 2, 3 and 4) and the unfunctionalized material (MCF) are displayed in Fig. 2. All samples exhibited a type IV isotherm behavior with steep hysteresis of type H1 at high relative pressures, indicating large mesoporous cells with a narrow pore size distribution (Schmidt-Winkel et al. 1999, 2000). The isotherms also show that the relative pressure, at which capillary condensation (i.e., mesopore filling) occurs, shifts systematically to lower relative pressure as the dendrimer generation increases. This indicates a reduction of the mesopore diameter due to the growth of dendrimers inside the mesopores. The growth of dendrimers inside the mesopores as the dendrimer generation increases was also confirmed by the reductions of surface areas and pore volumes as listed in Table 1. The hysteresis loop in the nitrogen sorption isotherm for MCF/G4 still appeared, indicating that the mesopores were not completely filled, even by the 4th generation melamine based dendrimer. There is still unoccupied mesopore volume giving room for further generation growth. A previous report on mesoporous materials (SBA-15 and MCM-41) modified with melamine based dendrimer showed that the maximum number of dendrimer generation that could be grafted was 2 and 4 for MCM-41 and SBA-15, respectively (Acosta et al. 2004; Liang et al. 2008). This can be understood as a consequence of the difference in pore size between that reported for MCM-41 (4.2 nm) and SBA-15 (8.3 nm), and that of MCF used in this study (27.2 nm).

Organic loadings in these functionalized materials (MCF/G0, 1, 2, 3 and 4) were calculated from the weight loss determined by thermogravimetric analysis (TGA) as listed in Table 2. The organic loading increases as the dendrimer generation increases. This confirms the growth of dendrimers in the mesopores. The decomposition of the dendrimer functionalized samples starts at around 300 °C, whereas weight loss observed below 150 °C in all samples was associated with desorption of CO$_2$ and moisture (Fig. 3).

Elemental analysis results (see Table 2) also showed that the organic loading increased with increasing dendrimer generation, confirming further the growth of the dendrimers within the mesopores. However, the molar ratios of N/C and N/H from the elemental analysis results were lower than ratios expected for ideally propagated melamine-based dendrimers. This suggests that the propagation of the dendritic structures on the mesoporous surface deviated from the ideal, and that incomplete branch extension or crosslinked structures were formed on the mesopore surface (see Scheme 2). This is understandable because of steric hindrance within the mesopores. As a result of non-ideal propagation, the proportion of terminal amine groups was reduced, and the ratios of N/C and N/H were below those of the ideal structures.

CO$_2$ adsorption profiles of these functionalized materials (MCF/G0, 1, 2, 3 and 4) as a function of time at 20 °C, were determined by TGA (Fig. 4). The profiles clearly show a rapid increase in the sample weight after exposure of the sample to CO$_2$ for about the first 3 min, followed by a slow

Table 1 Summary of the structural properties of MCF, MCF modified by aminopropyl group and MCF modified by the dendrimers

	Surface area (m^2/g)	Pore volume (ml/g)	Pore size (nm)	Window size (nm)	Heat of adsorption (kJ mol^{-1})
MCF	584.29	2.1	27.2	14.2	37.1
MCF/G0	372.17	1.8	25.3	14.0	42.4
MCF/G1	333.36	1.5	23.9	13.1	44.8
MCF/G2	293.47	1.3	21.0	11.4	49.2
MCF/G3	192.11	1.0	18.9	10.2	53.7
MCF/G4	151.81	0.8	17.0	8.4	58.6

Table 2 Summary of TGA decomposition and elemental analysis results of MCF/G0-4

Tested materials	TGA Organic loading (wt%)	Elemental analysis Organic loading (wt%)	Theoretical		Experimental	
			N:C	N:H	N:C	N:H
MCF/G0	10.3	10.4	1:3.0	1:8.0	1:3.5	1:11.9
MCF/G1	25.1	24.9	1:1.3	1:2.6	1:1.4	1:3.5
MCF/G2	38.9	35.9	1:1.1	1:2.1	1:1.2	1:2.9
MCF/G3	45.1	43.7	1:1.0	1:2.0	1:1.2	1:2.5
MCF/G4	54.9	50.1	1:1.0	1:1.9	1:1.1	1:2.3

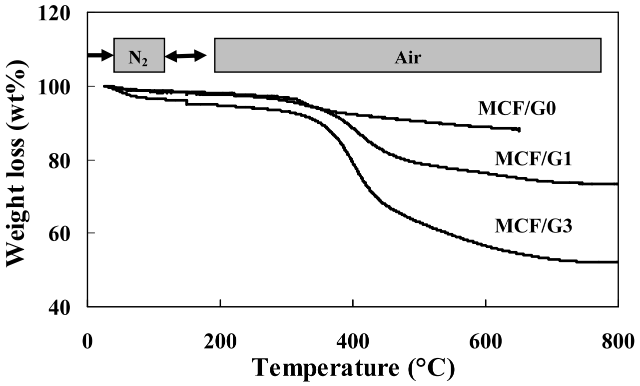


Fig. 3 Thermal decomposition of the functionalized MCF products

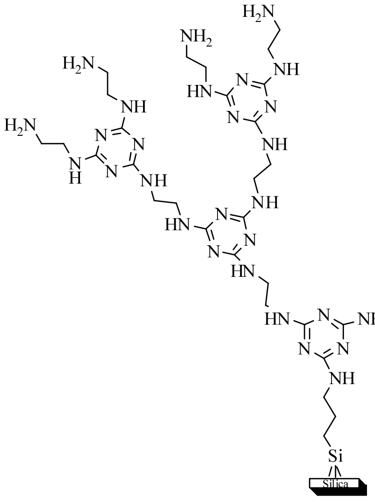
continuing uptake, which implies that the CO_2 adsorption capacities might be marginally better if adsorption times longer than 10 min had been employed, to enable samples to reach adsorption saturation.

The measured CO_2 adsorption capacities are shown in a bar graph (Fig. 5(a)). They are compared against the 'theoretical' values, calculated as previously described (Liang et al. 2008), assuming an adsorption stoichiometry of one CO_2 molecule for every 2 atoms of terminal primary amine. This is the stoichiometry requirement in the formation of ammonium carbamates under anhydrous condition (Kohl and Nielsen 1997). Although the melamine-based dendrimers also contain the weakly basic secondary (and aromatic nitrogen), they are apparently inactive toward CO_2 adsorption. The low reactivity of the secondary amines is probably due to their conjugation to the melamine ring which substantially reduces their basicity (Dean 1999). Therefore the dendrimer functionalized MCF samples show relatively low CO_2 adsorption capacities relative to other polymers, e.g. PEI and aminosilane functionalized mesoporous silicas (Xu et al. 2002; Harlick and Sayari 2007).

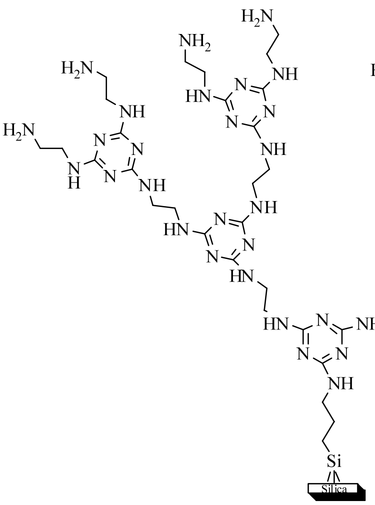
It can be seen that the experimental values for CO_2 adsorption are lower than the calculated 'theoretical' values. This can be rationalized if the actual number of primary amine groups present is less than expected due to non-ideal propagation of the dendritic structures (Scheme 2), an interpretation that is consistent with the elemental analyses. The figure also shows that the difference between the experiment and the theoretical becomes bigger as the dendrimer generation increases. This is understandable because of increasing steric hindrance within the mesopores.

Figure 5(a) shows that the CO_2 adsorption capacities of the dendrimer functionalized MCF are improved relative to the unfunctionalized MCF as a result of the addition of grafted amine functional groups. However, despite the increase in dendrimer loading with generation number, the adsorption capacity did not show a particular improvement when reported on a weight percentage basis (Fig. 5(a)). This is largely on account of the concomitant increase in the weight of the substrate (MCF) plus dendrimer (the denominator in the weight percentage calculation).

Recognizing that the dendrimer is grown on the mesopore surface of the MCF substrate and that the functionalized adsorbents created by this approach do not occupy any additional bulk volume, it is appropriate to recalculate and compare the CO_2 adsorption capacities as a percentage of the starting substrate (MCF) weight alone. This comparison is presented in Fig. 5(b), where it can be seen that the CO_2



A- Non-ideal propogation structure of MCF/G3



B- Non-ideal propogation structure of MCF/G3

Scheme 2 Illustration of possible non-ideal propagation structures of melamine based dendrimers in the mesopores, incomplete extension in MCF/G3 (A) and cross-linked MCF/G3 (B)

adsorption capacities do increase significantly with generation number to around 8.5 wt%. This is approximately a 3-fold improvement relative to the substrate alone. Of course, the experimental values still remain below the theoretical values, because of the non-ideal propagation of the dendritic structures.

The heats of CO_2 adsorption were determined by DTA are listed in Table 1. The heat of adsorption for unfunctionalized MCF was 37.1 kJ mol^{-1}, indicating the adsorption is essentially a physisorption phenomenon (no covalent bond formation). The heats of adsorption of the functionalized samples progressively increase with generation number from 42.4 to 58.6 kJ mol^{-1}, suggesting an increasing contribution from chemisorption (covalent bond formation). The high heat of adsorption (58.6 kJ mol^{-1}) for the most highly functionalized case (MCF/G4) is also consistent with the observation of incomplete CO_2 desorption—only 56 wt% of the adsorbed CO_2 was desorbed in 10 min at 20 °C. However, CO_2 desorption was fast and complete at 105 °C in the same period of time. These measured heats of adsorption of dendrimer-functionalized MCF samples are similar to those of dendrimer-functionalized SBA-15 samples reported previously (Liang et al. 2008) but, interestingly significantly lower than the heats of reaction reported for CO_2 with 30 wt% aqueous amine solvents e.g. monoethanolamine and diethanolamine, respectively (84 and 72 kJ mol^{-1}) (Kohl and Nielsen 1997). These lower values are probably beneficial from the perspective of a reduced energy requirement for adsorbent regeneration.

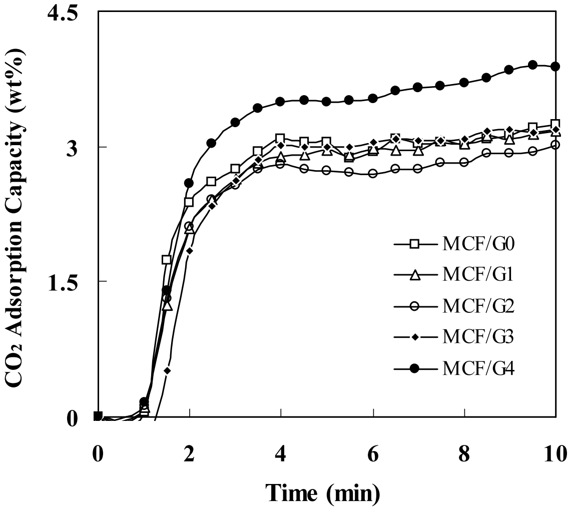


Fig. 4 CO_2 adsorption/desorption profiles of the samples of MCF/G0-4 as a function of time at 20 °C were determined by combined TGA/DTA

4 Conclusions

In summary, MCF containing ultralarge mesopores was used as substrate and functionalized with melamine-type dendrimers up to the fourth generation. The MCF mesopores were not completely filled by the dendrimer even at generation four, leaving some porosity available to facilitate rapid ingress and egress of small gas molecules. Thus MCF is an excellent substrate on which to graft macromolecular surface active groups—in this case, amine groups. Very high organic loading (54.9 wt%) were achieved. CO_2 adsorption experiments suggest that only the primary amines groups were active for CO_2 chemisorption in melamine-type dendritic structures, since the secondary and aromatic nitrogen groups have insufficient basicity.

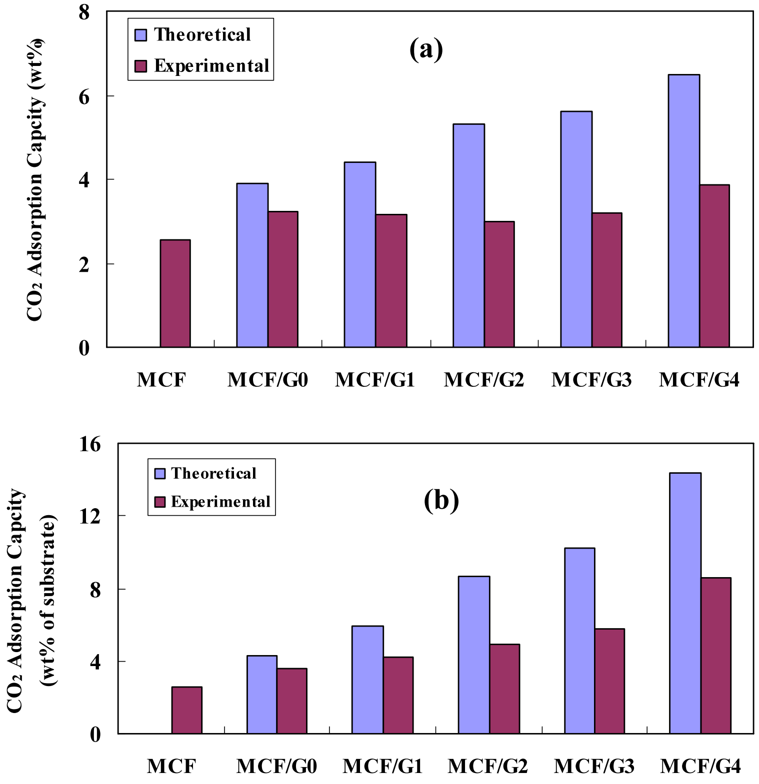


Fig. 5 Experimental and 'theoretical' values for CO_2 adsorption capacities of MCF and its functionalized products: (**a**) data are presented on a wt% basis, (**b**) data are presented on a wt% substrate basis

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