

ALTERNATIVE ROUTES IN THE SYNTHESIS OF AMINO FUNCTIONAL SORBENTS USING COMPRESSED CO₂

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ABSTRACT

Grafting of amines into porous silica has been extensively applied in the design of solid sorbents for reversible CO₂ adsorption processes. The synthesis of such materials is often performed using liquid solvents. In this work CO₂ technology, used as a supercritical (sc) fluid or in the low pressure compressed conditions, is shown as a promising alternative in the synthesis of amine based solid sorbents. Experiments were performed using the mesoporous MCM-41 as the solid support. On one hand, scCO₂ was used for the grafting of the aminosilane 3-(methylamino)propyl (MAP) on MCM-41. This process required the study of the optimal conditions to avoid the carbamate formation. A reaction temperature of 135 °C and 90 bar pressure were selected as the best conditions to obtain aminosilane grafting loadings in the range of 1.5-5.5 mmolg⁻¹. On the other hand, compressed CO₂ was applied in the synthesis of hyperbranched amino-polymer silica sorbent. In this case CO₂ was the activator of the ring-opening polymerization reaction of ethyleneimine monomer. In the order of minutes, pressures in the range of 60-100 bar and 45 °C, high aminopolymer loadings of polyethyleneimine (PEI) among 6-8 mmolg⁻¹ are obtained. Thermogravimetric analysis (TGA) was used to estimate loading amounts as well as to study the thermal stability of the synthesized products. Similar decomposition temperatures around 200-250 °C were found for aminosilane and PEI samples. N₂ adsorption measurements were applied in order to understand the final textural properties after the functionalization of the mesoporous MCM-41. CO₂ adsorption isotherms were used to study the overall adsorption capacity and the chemisorption and physisorption branches of the synthesized sorbents. At 25 °C adsorption values in the range of 1-2 mmolCO₂g⁻¹ are found for aminosilane samples and 0.5-1.5 mmolCO₂g⁻¹ for the PEI sorbent. The effect of the temperature on the CO₂ adsorption isotherm was studied at 25, 75 and 110 °C.

INTRODUCTION

The use of liquid amines for the absorption and separation of CO₂ from fossil-fuel-burning emissions has been a commonly used approach. However, there are several problems associate to the use of liquid amines, such as the degradation and evaporation due to applied absorption/desorption cycles, where amines are constantly exposed to relatively high temperatures. Moreover, high energy costs are required to heat liquid amines dissolved in aqueous media. In order to avoid these limitations, several efforts are currently being done in

the development of solid sorbents where amines are attached to the surface of mesoporous silica [1]. Heating costs, degradation and evaporation become less of an issue if amines are grafted on the surface of a solid.

Several reasons have made mesoporous silica to become one of the best candidates for the incorporation of host molecules into the pores. The wide range of pore sizes and the presence of silanol (-OH) groups on the surface of silica made possible the grafting of host molecules with different sizes.

Aminosilanes are among the preferred amine candidates to be grafted on mesoporous silica due to the presence of the silane group, which can establish covalent and hydrogen bonds with hydroxyls on the silica surface, hence, providing a high thermal stability. Other organic molecules containing amino groups have also been grafted on the surface of mesoporous silica. This is the case of aminopolymers such as PEI, organic polymers with a higher amino group density than aminosilanes, which may be advantageous in CO₂ adsorption applications. Polyethyleneimine (PEI) is used due to its high content of amino groups with respect to the carbon content. In the case of PEI, two ways of introducing the polymer into mesoporous silica have been designed. The simplest approach is the wet impregnation method, where PEI polymer is dissolved in an organic solvent and brought into contact with the porous substrate. Reaction time and temperature may help the impregnation of the polymer into the pores. A different approach is based on the in situ polymerization of ethyleneimine (commonly known as aziridine, AZ) monomer in solution and with the aid of a catalyst such as acetic acid. The ring-opening polymerization of ethyleneimine leads to the formation of a hyperbranched polymer with secondary, tertiary and primary amines in its chemical composition.

Common methods for grafting aminosilanes and amino polymers into mesoporous silica require a liquid-phase deposition step, with significant amounts of organic solvent waste. Moreover, oligomerization in solution is often a non-desired side reaction of the liquid deposition method, because it can affect negatively the surface coverage homogeneity. Other methods, such as chemical vapor deposition (CVD) or vapor-phase transport are limited to volatile and thermally stable aminosilanes and usually require high temperatures over long reaction times [2, 3]. In several works, scCO₂ has been used as a solvent in the silanization of porous silica using alkylsilanes. Results showed that scCO₂ is one of the most effective, simple and reproducible methods for producing homogeneous, covalently bonded, high density silane films on the internal surface of porous materials. For the specific application of coating of nano and microporous supports, the use of scCO₂ as a solvent has the advantage of its gas-like diffusivity and zero surface tension, allowing the easy penetration of the fluid into the pores and the complete wetting of intricate geometries. Moreover, the waste stream, inherent to the organic solvents preparation, is eliminated. Covalent bonding of organosilanes onto oxide supports using the supercritical method has been extensively scrutinized in the past in our laboratories. In previous studies, the supercritical silanization with alkyltrialkoxysilane of several micro and mesoporous silica supports was deeply analyzed [4, 5]. The present work examines the functionalization of mesoporous silica MCM-41 with two amine-based organic molecules: aminosilanes and ethyleneimine monomer.

MATERIALS AND METHODS

The aminosilane 3-(Methylamino)propyl (MAP) (Sigma-Aldrich) with 106 °C boiling point, was used as grafting solute in the supercritical silanization process. Dry ethanol (Et) and ether (Eth) obtained from Panreac were used as cosolvents. The three membered ring ethyleneimine (Menadiona S.A) was used for the ring-opening polymerization under compressed CO₂. The silanization process was performed into the mesoporous silica MCM-41 (MCM-41,ACS Materials). MCM-41 was boiled in distilled water at 100°C for 1h to increase the surface silanol density to 3 OHnm⁻² and then dried in an air-oven at 120 °C overnight before use. CO₂ (99.9999%, Carburos Metálicos S.A.) was used as the reaction media in both processes.

The extent of mixing of MAP with CO₂ was essential information necessary to settle the operating conditions of pressure and temperature in the supercritical silanization process. The reaction between amines and CO₂ to form carbamates is a reversible process with a high dependence on the reaction temperature. The qualitative description of the behavior of MAP with temperature and CO₂ pressure is described elsewhere [6]. Experiments with MAP were performed at temperatures of 75 and 100 °C and pressures of 75 and 90 bar. Some of the experiments were performed adding 2-5%v of Et. or Eth. as a cosolvent.

The supercritical silanization was performed using a set-up depicted in figure 1. In a general procedure, a reactor vessel with a volume of 100 mL (Autoclave Engineers) is charged with ca. 0.3 g of substrate enclosed in a cylindrical cartridge made of 0.45 µm pore filter paper, placed in the upper part of the autoclave. Liquid MAP (ca 1mL) was then added to the bottom of the reactor with a volume of cosolvent. Befor the addition of compressed CO₂ the reactor is heated at 100 °C applying a moderate vacuum during 20 min to eliminate water from the system. After, compressed CO₂ is added up to the desired pressure (P) once the equipment is heated and stabilized at the chosen temperature (T).

The performance with ethyleneimine polymerization was done following a similar procedure to MAP. Once the ethyleneimine is placed at the bottom of the reactor the vessel is heated to 45°C and pressurized to the desired pressure (60 and 100 bar in these experiments). After 10 min of reaction time the vessel is depressurized and cooled down.

In order to estimate the amount of organic loading as well as the thermal stability of the modified silica thermogravimetric analysis (TGA) was performed under a 25 ml/min N₂ flow using a TGA Instrument Q5000 IR and at a heating rate of 10 °Cmin⁻¹. In some samples organic elemental analysis of C, N and H was performed with a Flash EA2000 Thermo Fischer Sci. Textural characteristics and physisorption capacity of raw and functionalized substrates were studied by low temperature N₂ adsorption/desorption analysis (ASAP 2000 Micromeritics). Prior to measurements samples were dried under reduced pressure at 120 °C for 20h. The specific surface area (S_a) was determined by the BET method, the mesopore volume (P_v) was calculated using the BJH method with the adsorption branch of the isotherm. Sorption isotherms of CO₂ were obtained using a Micromeritics ASAP 2020 analyzer in the interval of 0-100 kPa. Prior to measurements samples were outgassed under reduced pressure following the same procedure than that of N₂ adsorption. A circulator bath containing heated oil was used to obtain the isotherms at different temperatures.

RESULTS

The scheme from figure 1 represents the two synthesis pathways using supercritical CO₂ for 3-(methylamino)propyl silane (MAP) (M1) and compressed CO₂ to obtain PEI (M2). In M1 method CO₂ is the solvent media for MAP, which is covalently attached on mesoporous MCM-41. M2 shows the mechanism of functionalization with ethyleneimine monomer under compressed CO₂. In this case CO₂ is used as the reaction media and the catalyst of the ethyleneimine ring-opening polymerization that leads to hyperbranched PEI.

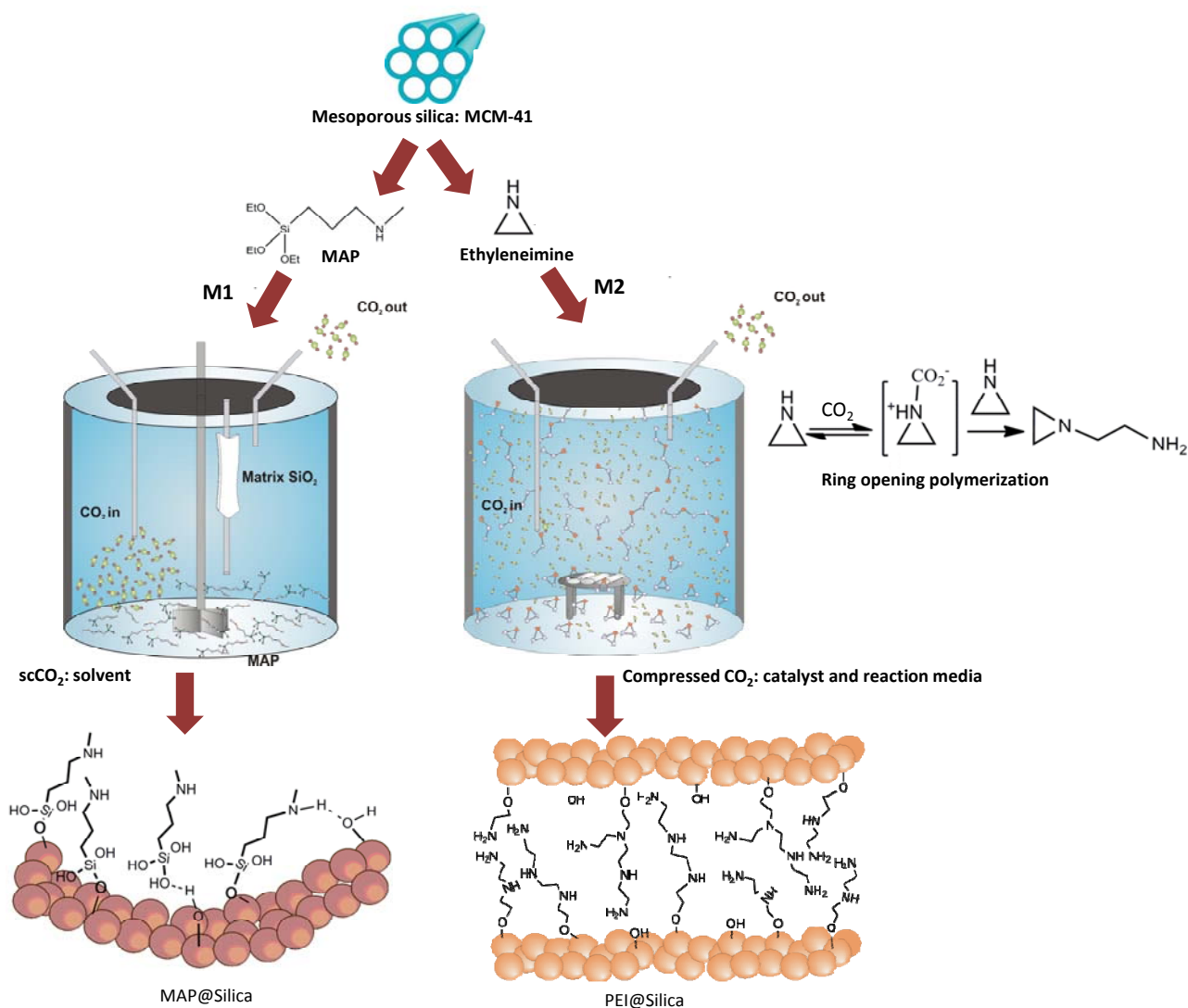


Figure 1. Schematic representation of the method to functionalize MCM-41 with aminosilane MAP using supercritical CO₂ (M1) and with hyperbranched PEI through the polymerization of ethyleneimine under compressed CO₂ (M2).

The mesoporous MCM-41 has a periodic pore structure organized in one-dimensional (1D) arrays of non-intersecting hexagonal channels. Textural properties of MCM-41 for bare and modified samples are summarized in table 1 together with the operating conditions for each experiment.

Table 1. Operation conditions for synthesized samples and amine density expressed in mmolN per gram of product.

Sample	Amine type	T [°C]	P [bar]	Cosolv. [%v]	ρ [mmolNg ⁻¹]	S_a [m ² g ⁻¹]	P_v [cm ³ g ⁻¹]
MCM-41	-	-	-	-	-	1127	0.92
A-MAP@MCM	MAP	135	90	Eth 2%	1.5	457	0.40
B-MAP@MCM	MAP	135	90	Eth 5%	5.4	10	0.01
C-MAP@MCM	MAP	135	90	Et 2%	2.1	681	0.57
A-PEI@MCM	AZ	45	60	-	6.0	306	0.21
B-PEI@MCM	AZ	45	100	-	8.0	49	0.07

M1 synthesis route uses MAP, a silylating coupling agent with a secondary amine in its structure. The reaction of CO₂ with primary and secondary amines leading to carbamates is usually described by the zwitterion mechanism. The carbamation is a reversible process highly dependent on the temperature and CO₂ pressure. In a previous work we evaluated the optimal operating conditions required to have free aminosilane in solution by studying the phase behavior of the system scCO₂/aminosilane at different pressures and temperature [6]. Minimum working conditions were selected at 135 °C and 90 bar.

M2 route corresponds to the ring opening polymerization of aziridine where a different mechanism requiring low temperatures and CO₂ pressures is followed [7]. It has been stated that unsubstituted aziridine reacts with CO₂ to give a homopolymer in the absence of the other catalyst, i.e., CO₂ is not incorporated into the polymer [8].

Thermal behavior of the functionalized samples was studied by thermogravimetric analysis. For MAP loaded MCM the weight decay tendencies observed in the TGA profiles shows a first decay up to 100 °C corresponding to the desorption of physically adsorbed water from the matrix and CO₂ from the amine decarbamation. The release of hydrolyzed unreacted molecules of aminosilanes occurred in the interval from 100 to 250°C. The decomposition of grafted alkylamine occurs above 250 °C and up to 600-650 °C.

In the case of polymerized aziridine, PEI, thermal decomposition of the polymer occurs in the range 200-500 °C with the highest derivative peak at *ca.* 340 °C. This corresponds to the highest decomposition temperature found in the literature for similar products synthesized following the conventional routes [7].

The weight loss data from TGA profiles was used to calculate the grafting density per gram of dry substrate. For the MAP samples, the molecular weight of grafted aminosiloxane decomposing at temperatures higher than 250 °C is considered (CH₂)₃NHCH₃ =72) whereas CH₂CH₂NH=43 is considered for PEI calculations. Data obtained from TGA measurements was corroborated with the values obtained from elemental analysis indicating the validity of the selected intervals of temperature used to calculate the weight loss of the species.

It is expected that the principal reaction occurs between the surface silanols on the silica and the alkoxy portion of the aminosilane molecule (not the amine). Hence, aminosilanes are deposited on the surface via reaction with silanols (covalent bonding) or siloxane bridges (hydrogen bonding).

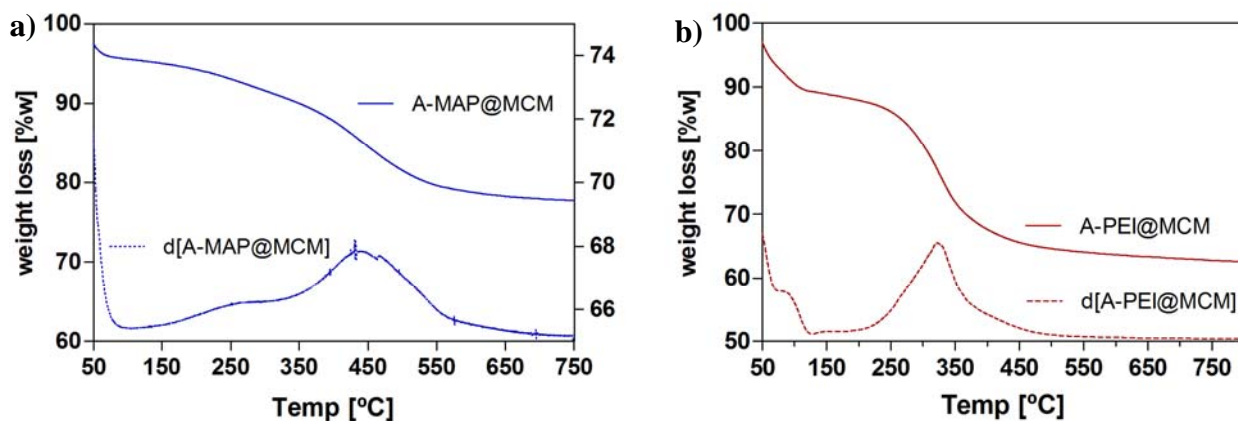


Figure 2. Thermogravimetric and weight derivative profiles for A-MAP@MCM (a) and A-PEI@MCM (b).

N_2 adsorption isotherms of the raw substrates are compared to the respective functionalized samples. The BET surface area and pore volume of the raw and modified substrates are listed in Table 1. MCM bare material exhibited type IV isotherm. The unmodified MCM exhibited a sharp step of capillary condensation in primary mesopores at the relative pressure of *ca.* 0.5, indicating a narrow pore size distribution of the material. For the studied supports the surface area and pore volume decreased after the modification.

For MCM samples with 1.5-2.1 mmolN g⁻¹ and 6 mmolN g⁻¹ of MAP and PEI, respectively, the available pore volume decreased in *ca.* 50 %. MAP and PEI loadings up to 5.4 and 8.0 mmolNg⁻¹, respectively, implied a total drop in the sample pore volume, attributed to pore blocking at least for N_2 adsorption.

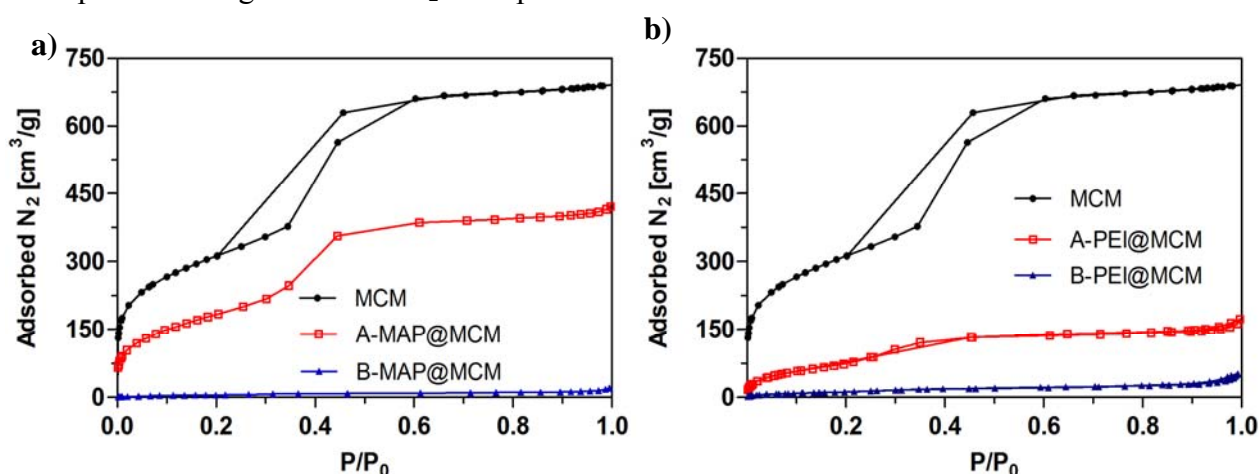


Figure 3. N_2 adsorption isotherms for MAP@MCM (a) and PEI@MCM (b) samples.

Adsorption of CO_2 with primary and secondary amines it is based on the as mentioned reversible carbamate formation. The exothermic acid-base reaction strongly depends on the temperature and CO_2 pressure. The CO_2 adsorption of the synthesized samples was studied by using adsorption isotherms. Figure 4 shows CO_2 isotherms for MAP@MCM samples. On

figure 4a MCM-41 bare material shows the lowest adsorption due to the absence of interaction between silica surface with CO₂. The sorption increased to values of ca. 1.5 and 2.9 for B-MAP@MCM and A-MAP@MCM respectively. In the chemisorption region, occurring at low pressures below 15 kPa, A-MAP@MCM has an adsorption value of 1.0 mmolN/g whereas adsorption in B-MAP@MCM is about 50% higher. This is due to the higher amino group's density (5.4 mmolN/g) in B-MAP@MCM than in A-MAP@MCM (1.5 mmolN/g).

Figure 4b shows the CO₂ adsorption isotherms of A-MAP@MCM at different temperatures (25, 75 and 110 °C). The best performance occurred at room temperature with the maximum theoretical adsorption efficiency of 0.5 reached (2 moles of amines are required to react with 1mol of CO₂). When the temperature was elevated to 75 °C the adsorption efficiency dropped to 0.38. By further increasing the temperature to 110 °C the chemisorption was not observed and the adsorption profile was similar in shape to that of the raw material.

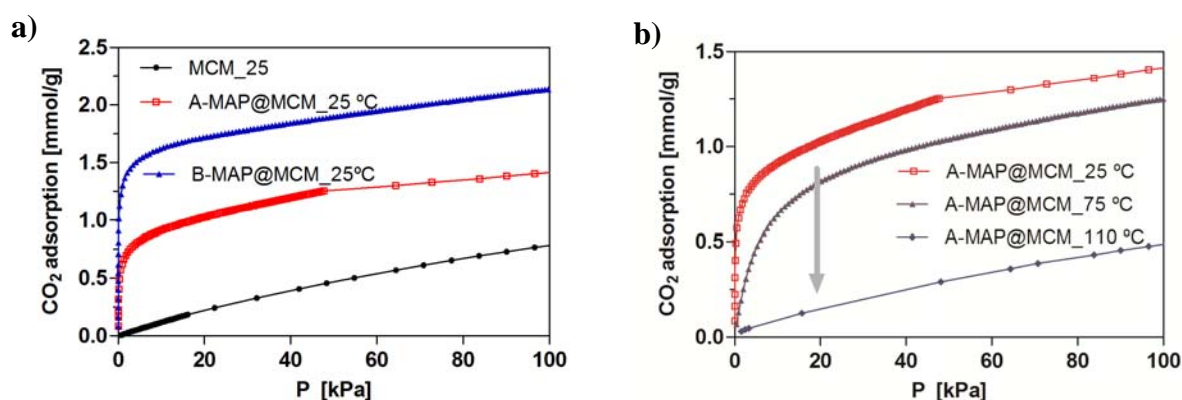


Figure 4. CO₂ adsorption isotherms at 25 °C (a) and at various temperatures (25, 75 and 110 °C) for MAP@MCM samples.

Isotherms for A-PEI@MCM and B-PEI@MCM at 25 °C and 75 °C are shown on figure 5. Although samples B-PEI@MCM and B-MAP@MCM exhibited pore blocking for N₂ adsorption (figure 3) it did not hinder the CO₂ adsorption at both studied temperatures. Moreover, isotherms at both temperatures showed a high CO₂ adsorption even at low CO₂ pressures. This apparent contradiction is related to the higher temperature used for the CO₂ adsorption measurements compared to the -196 °C used for N₂ adsorption, at which PEI and MAP chains are expected to behave as rigid materials. At 25 °C, the A-PEI@MCM sample showed a CO₂ adsorption value of 1.56 mmol CO₂ per g at 100 kPa, which is nearly twice the capacity of the A-PEI@MCM sample under similar conditions, 0.89 mmol CO₂ per g. Increasing the temperature to 75 °C resulted in a significant enhancement in the CO₂ adsorption of the highly loaded sample B-PEI@MCM to a value of 1.43 mmol CO₂ per g. The opposite behavior was observed for A-PEI@MCM: the adsorption capacity was reduced to 0.89 mmol CO₂ per g by increasing the temperature. The increase of the temperature is expected to affect CO₂ adsorption in two mutually divergent ways. First, adsorption is enhanced by increasing polymer mobility and CO₂ diffusivity. Second, adsorption is hindered by shifting the equilibrium of the carbamate formation in the exothermic reaction (Fig. 1c). For sample B-PEI@MCM, with potential pore blocking, the increase in CO₂ diffusivity with temperature seemed to be the principal effect and, thus, CO₂ adsorption was enhanced by increasing the adsorption temperature. In contrast, for sample A-PEI@MCM, CO₂ adsorption

diminished with a similar temperature increase, which fundamentally worked against the formation of carbamate molecules.

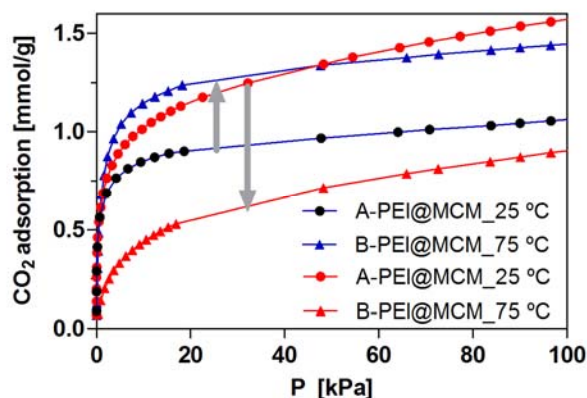


Figure 5. CO₂ adsorption isotherms at 25 °C and 75°C for PEI@MCM samples-

CONCLUSIONS

Compressed CO₂, either supercritical or compressed at low pressure, are proposed here as a promising alternative on the synthesis of amino silica sorbents for CO₂ adsorption purposes. On one side, supercritical CO₂ has been used for the grafting of an aminosilane into MCM-41 obtaining high grafting densities from 1.5 up to 5.4 mmolN/g. On the other side, compressed CO₂ was applied in the polymerization of aziridine, obtaining loading values between 6 and 8 mmolN/g into MCM-41. Both type of materials present a high thermal stability with decomposing temperatures up higher of 250 °C. CO₂ adsorption performance under various temperatures showed an expected behavior with adsorption values between 1.0 and 2.0 mmolCO₂g⁻¹.

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