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CO_2 Capture at Low Temperature by Nanoporous Silica Modified with Amine Groups

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MCM-41 and SBA-15 were chosen as nanoporous materials based on silica for its modification with amine groups. This modification was done by two methods: grafting method and wet impregnation method. The first method grafted-amine groups by chemical reaction between surface silanol groups in the nanoporous materials and 3-aminopropyltrimetoxilane (APTMS).In the wet impregnation method, low molecular weight polyethylenimine (PEI) is incorporated trough this method. These modified materials capture CO_2 at low temperature. CO_2 capture on the sorption sites by amine loading is believed to occur via chemisorption mechanism by formation of ammonium carbamate. The evaluation and analysis of CO_2 adsorption was carried out by two methods: static mode and dynamic mode. The static mode is a pure CO_2 adsorption-desorption isotherms at 298K. The isotherms of the functionalized materials show a behavior by chemisorption, capture at low pressure, being the desorption branch almost horizontal, while nanoporous silica isotherms is due a physical adsorption, low CO_2 capture at low pressure and dependence with pressure, a complete reversibility of the desorption process. The dynamic mode is a thermogravimetry study at different N_2/CO_2 concentrations. Isothermal CO_2 captures at 298K were carried out to evaluate the suitability of the samples for cyclic operation. The mass increase during the capture step was interpreted as CO_2 adsorption capacity of the samples. The results obtained by both methods were compared, and, its differences were analyzed.

1. Introduction

Carbon dioxide emissions from fossil combustion have attracted more concern due to its important impact on the atmosphere. Several methods have been proposed to capture CO_2. Also, several materials have been used for this purpose such as porous adsorbents, mesostructured solid, zeolites, metal oxides, metal-organic frameworks (MOF), (Chen et al., 2014). Amine groups can potentially enhance CO_2 chemisorption interaction with CO_2/N_2. Moreover, nanoporous materials can be modified with amine groups and can potentially improve the performance of this interaction, (Chen et al., 2014); (Liu et al., 2015).

In the last years, different amine-modified solid sorbents have been worldwide developed for CO_2 capture and separation, and many review depicted the progress of their search (Wang et al.,2011), (Samanta et al., 2012) and (Kaithwas et al., 2012). Amine-modified sorbents solid supports with highly developed porosity and active sites have high affinity for CO_2. MCM-41 and SBA-15 have been the most studied porous silica due to their larger pore size, and thermal, mechanical and chemical resistance. Mainly, two methods are employed to prepare amino sorbents, impregnation and grafting. Grafting is based on a chemical reaction between silanol groups, present on the silica porous surface, and aminoxilane molecules. These organic molecules are covalent bonded to the surface of the porous giving rise to amine porous silica with high selectivity towards CO_2. For impregnated method, CO_2 adsorption capacity can be achieved by loading varying amounts of amine polymers inside the pores, polyethyleneimine (PEI) is one of the most commonly used (Sanz et al., 2015).

CO_2 adsorption with amines sites is believed to occur via chemisorption mechanism, forming zwitter-ion and ammonium carbamate as a final product. CO_2 adsorption involves two nitrogen atoms per CO_2 molecules.

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Primary and secondary amines react with CO_2 to produce carbamate via zwitter-ion mechanism, (Vilarrasa-García et al., 2015).

In this work, 3-aminopropyltrimetoxilane is used for the grafting method and polyethylenimine is used for the impregnation method on pure siliceous hydrothermal MCM-41 and SBA-15 nanoporous materials. The analysis of the CO_2 adsorption was evaluated by two methods: static and dynamic mode. The static mode was carried out by pure CO_2 adsorption-desorption isotherms at 298 K with pressure from 0-1bar, the outgassing steps at 383K under vacuum for 6h were carried out before each analysis. For the dynamic mode a thermogravimetry study at different N_2/CO_2 concentrations were carried out. Isothermal CO_2 capture at 298 K were carried out to evaluate the suitability of the samples for cyclic operation. The results obtained by both methods were compared and analyzed.

2. Experimental

2.1 Amino grafted and amino impregnated silica materials

Mesoporous silica materials were prepared using different types of surfactant molecules as a template and different sources of silica as precursor in an aqueous medium. MCM-41 was obtained using fumed silica and sodium silicate solution as source of silica, and hexadecyltrimethyl-ammonium bromide as template, tetramethylammonium hydroxide was used as base medium. SBA-15 was obtained with tetraethyl orthosilicate (TEOS) as silica source, copolymer triblock Pluronic (P123) as template and HCl as acid medium, (Meynen et al., 2009).

The grafting agent was 3-aminopropyltrimetoxilane (APTMS). In a typical experiment 1.0 g of nanoporous material (MCM-41 or SBA-15), previously pretreated at 423K for 2 h and dispersed in 50 ml of dry toluene, a is added to a calculated amount of APTMS (4, 20, 40 mmoles/g as SBA-15 support and 5, 7.5, 10 mmoles/g as MCM-41 support). After that the suspension was stirred and refluxed for 24 h under nitrogen atmosphere. The functionalized products were recovered by filtration, washed with toluene and dried at 283K for 24 h in oven. The materials were named as MCM41(x) or SBA15(x) where (x) represents the mmoles of APTMS per g silica support.

In addition, silica materials were functionalized by impregnation method with low molecular weight (650 MW) polyethylenimine (PEI). Organic amounts of 20, 40 and 60 % were loaded in the porous structure of MCM-41 and SBA-15 using ethanol as solvent, silica: ethanol weight ratio of 1:5. In a typical experiment 1.0 g of nanoporous material (MCM-41 or SBA-15), previously pretreated at 423K for 2 h and dispersed in 5 ml of ethanol, was mixed with the appropriate amount of PEI and maintained under stirring for 30 minutes. The product was dried at 333K for 24 h in oven. The materials were named as PEI-MCM41(y) or PEI-SBA15(y) where (y) represents the percentage of PEI incorporated in the sample.

2.2. Characterization

Adsorption-desorption isotherms at 77K were acquired in a Micromeritics Asap 2010. A degasification step for 24h at 213K under vacuum for siliceous materials and for organic-containing materials was carried out before each isotherm. The specific surface area was obtained by BET equation in the range P/P^o from 0.05 to 0.20 (Gregg et al., 1982). The pore size distribution was obtained by means of the BJH method from adsorption branch of the isotherms (Barrett et al., 1951).

The organic content loaded in the materials was determined by thermal analysis in a Setaram Setsys Evolution-1700, TG-DSC coupled to a mass spectrometer Balzers OmniStar for evolved gas analysis. The samples of approximately 10 mg were heated in platinum crucibles in air atmosphere, at a total flow rate of 20 $ml.min^{-1}$, with a heating rate of $10ºC.min^{-1}$ and a final temperature of 1073K . All the TG measurements were blank curve corrected.

2.3 CO_2 adsorption-desorption measurement

The CO_2 adsorption-desorption isotherms were carried out at 298K with pressure from 0 to 1 bar in a Micromeritics Asap 2010 instruments. The outgassing step at 383K under vacuum for 6h was carried out before each analysis. The CO_2 used in the isotherms is pure.

The isothermal CO_2 capture at 298K of the amino functionalized materials was evaluated in a Setaram Setsys Evolution-1700 thermogravimetry analyzer. Samples were pretreated under N_2 at 383K for 30 minutes. Then, after reaching the desired temperature, the N_2 atmosphere is changed to $N_2/CO_{2,}$ (ratio 1:10) to a flow of 20 $ml.min^{-1}$, for 2h or 6h. To evaluate the suitability of the samples for cyclic operation, each CO_2 capture at 298K was followed by regeneration at 110 °C under nitrogen for 30 minutes. Then, the process was repeated for CO_2 capture at 298K under N_2/CO_2 under the same conditions. Each capture-regeneration cycle was repeated two or six times. The mass increase during the process of CO_2 capture is interpreted as the CO_2 adsorption capacity of the samples.

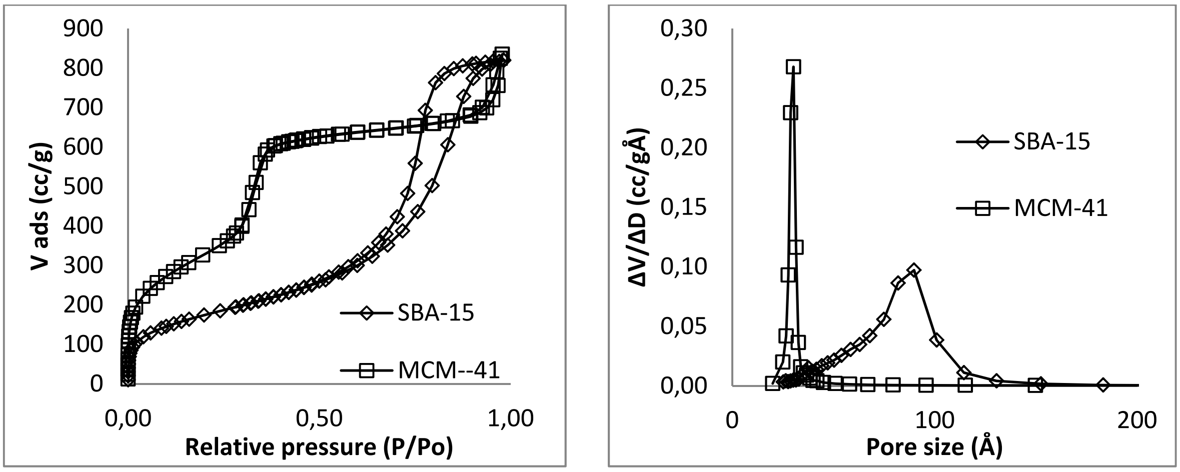

Figure 1: Left, N_2 adsorption- desorption isotherms at 77K of the raw samples: SBA-15 and MCM-41. Right, pore size distribution of the raw samples: SBA-15 and MCM-41.

3. Results and discussion

N_2 adsorption-desorption isotherms of the siliceous materials MCM-41 and SBA-15, and the pore size distribution obtained by means of the BJH method are represented in Figure 1. The surface area of all the materials was evaluated using BET method, and their textural properties are summarized in Table 1.

The nitrogen adsorption-desorption isotherms of MCM-41 and SBA-15 (Fig.1, left) show type IV isotherm with a sharp step up in a narrow range of relative pressures (P/P^o = 0.25-0.40 and 0.68-0.75) arising from the capillary condensation of nitrogen in the mesopores. MCM-41 sample has mean pores radius lower (1.5 nm) than the SBA-15 (6.5 nm).

All the amino functionalized samples show a decrease in the specific surface area, pore volume and pore diameter (Table 1). Such significant decrease of the textural properties of the grafted samples is due to the pore filling, which blocks the pores. The loaded organic content in the materials was determined by thermal analysis in air atmosphere. The percentage of organic matter incorporated in the samples is shown in Table 1. In both synthesis process, grafted aminoxilane (APTMS) and impregnation with PEI, a decrease in textural parameters agrees with an increase in the content of organic molecules on the sample surfaces.

To determine the CO_2 adsorption properties, pure CO_2 isotherms on the samples at 298K were obtained, some of them are shown in Figure 2. The isotherms of the raw materials, (Fig. 2, left), present a behavior, due to a pure physical adsorption, of a low CO_2 capture at low pressure and a strong adsorption with increased pressures, associated with the raw materials high specific surface, as well as a complete reversibility in the desorption process.

In the isotherms of the amino-functionalized samples, (Fig. 2, right), the CO_2 capture is very high at low pressure due to the appearance of a much stronger adsorption in the amino-functionalized materials. The isotherms present hysteresis due to the strong interaction between amine and CO_2, this is a chemisorption process, leading to an incomplete desorption of CO_2. The CO_2 adsorption in samples is irreversible, being the desorption branch almost horizontal.

In Table 2 the CO_2 adsorption capacity of samples at 1.0 and 0.1 atm obtained from the isotherms of CO_2 adsorption at 298K are shown. The raw materials (SBA-15, MCM-41) present a wide difference between the adsorbed CO_2 at 1.0 and at 0.1 atm, due to the weak interaction, physisorption, between the CO_2 and these materials.

Table 1: Specific surface area of amino functionalized samples and percentage of organic matter incorporates in amino functionalized samples.

Sample	S_{BET} (m^2/g)	% (mass)	Sample	S_{BET} (m^2/g)	% (mass)
SBA-15	530	----	MCM-41	1186	----
SBA-15(4)	145	15.3	MCM-41(5)	224	17.1
SBA-15(20)	67	17.4	MCM-41(7.5)	118	18.7
SBA-15(40)	5	29.4	MCM-41(10)	63	20.7
PEI-SBA-15(20)	239	18.8	PEI-MCM-41(20)	783	17.2
PEI-SBA-15(40)	96	35.0	PEI-MCM-41(40)	208	36.8
PEI-SBA-15(60)	15	53.3	PEI-MCM-41(60)	26	57.8

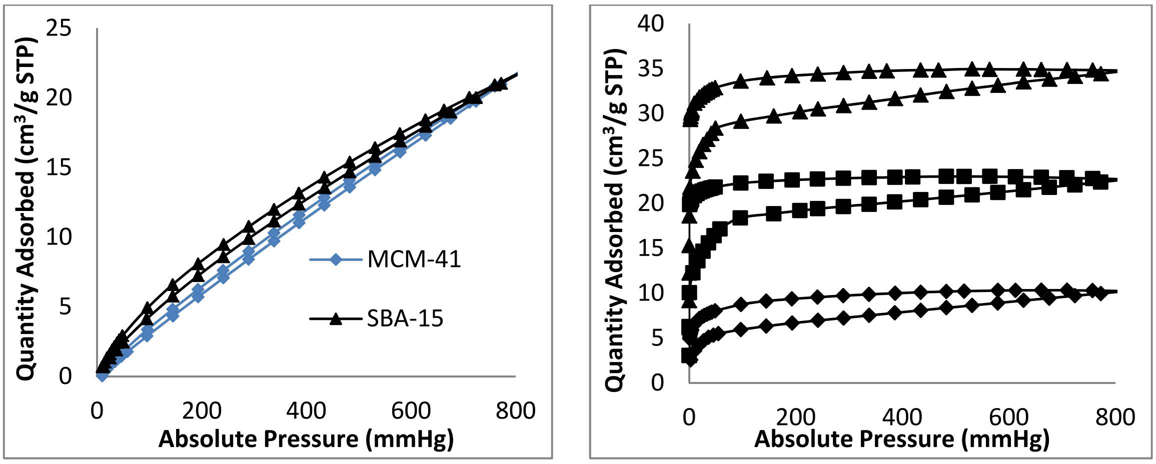

Figure 2: Left, CO_2 adsorption- desorption isotherms at 298K of (♦)MCM-41 and (▲)SBA-15. Right, CO_2 adsorption- desorption isotherms at 25ºC of (♦)PEI-SBA-15(20), (▲)PEI-SBA-15(40) and (■)PEI-SBA-15(60)

However, the functionalized materials show that the difference between the two pressures intervals is smaller. This is because a stronger interaction, chemisorption, between CO_2 and the actives sites of amino-functionalized mesoporous silica. This stronger interaction is due to the reversible formation of ammonium carbamates and/or carbonates during CO_2 adsorption (Yokoi et al., 2012).

The amino grafted materials on SBA-15 sample with greater adsorption of CO_2 at 1.0 atmosphere (45.5 cm^3/g) is the one with lower content of organic matter, SBA-15(4). While the amino grafted material on MCM-41 shows greater adsorption (39.1 cm^3/g) with higher content of organic matter, due to their higher surface area and therefore greater incorporation of active centers on its surface.

Impregnated SBA-15 materials with poliethylenimine (PEI) have higher levels of adsorption (34.4 cm^3/g) than impregnated MCM-41 materials, due to their larger pore size. The MCM-41 small pore sizes cause polymer blockade of the pores in a greater extension with a lower percentage of PEI incorporation (18.1 cm^3/g).

Moreover, in some samples of each method of functionalization, CO_2 capture was also followed by a flow of N_2/CO_2 gas mixture at different concentrations in a thermobalance (conditions in section 2.3).

The capture was monitored by the mass increase of its samples when the samples were exposed to CO_2. The capture capacity is expressed as weight percentage of the final materials. To evaluate the suitability of the samples for cyclic operation, the samples were followed by regeneration at 383K under nitrogen for 30 minutes. Then, the process was repeated for CO_2 capture under the same conditions.

The two cycles are shown in Figure 3-left for the sample MCM-41(7.5). A strong adsorption is observed in the first minutes due to the chemisorption with the amino groups.

Then, there is shown a continuous upward tendency for 120 minutes of the capture step and without reach the equilibrium capacity. In table 3, the maximum capture is shown in percentage of CO_2 mass in the first and second cycle. The CO_2 capture in the second cycle is always lower than the first one. This fact indicates that regeneration is not fully complete in any sample. This is due to the contribution of chemisorption process which hinders regeneration in first cycle. But, as shown in Figure 4, after six cycles of regeneration-capture in the MCM-41(7.5) sample, the captured CO_2 remain almost constant (4.0 % CO_2) between the second and sixth cycle.

Table 2: CO_2 adsorption capacity of samples at 1.0 and 0.1 atmosphere (atm), obtained from the isotherms of CO_2 adsorption at 298K.

Sample	CO_2(1.0 atm) cm$^{3/}$g	CO_2(0.1 atm) cm$^{3/}$g	Sample	CO_2(1.0 atm) cm$^{3/}$g	CO_2(0.1 atm) cm$^{3/}$g
SBA-15	20.8	3.5	MCM-41	20.7	2.1
SBA-15(4)	45.5	34.3	MCM-41(5)	29.5	22.1
SBA-15(20)	23.2	15.2	MCM-41(7.5)	33.5	27.6
SBA-15(40)	3.1	0.9	MCM-41(10)	39.1	29.4
PEI-SBA-15(20)	9.9	5.7	PEI-MCM-41(20)	6.3	4.1
PEI-SBA-15(40)	34.4	29.0	PEI-MCM-41(40)	7.0	4.4
PEI-SBA-15(60)	22.3	18.0	PEI-MCM-41(60)	18.1	11.9

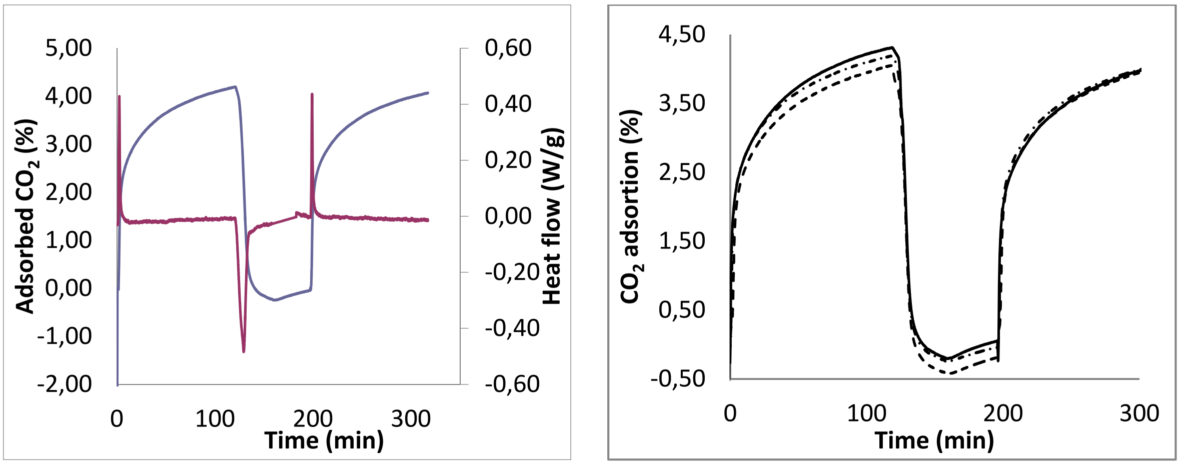

Figure 3: Left, Isothermal (298K) CO_2 capture-regeneration cycle two times of MCM-41(7.5) sample and DSC signal. Right, Idem, CO_2 capture using different percentages of CO_2 in the gas flow 5 % (---),10 % (-··-) and 20 % (—)

The selected temperature is room temperature because a higher temperature will act to the detriment of capture, due to exothermic chemisorptions process in CO_2 capture by amine groups of functionalized materials, (Plaza et al., 2007). In Figure 3-Left DSC show exothermic signals, these are observed in the CO_2 capture processes in both cycles, and show an endothermic signal in the regeneration step of the material.

The CO_2 capture results obtained by thermogravimetry, Table 3, are consistent with those obtained by CO_2 isotherms, considering that a procedure is in a static regime with pure CO_2 and the other is in a dynamic flow regimen and a rate of 10 % CO_2.

In the MCM-41(7.5) sample was evaluated CO_2 capture using different percentages of CO_2 in the gas flow (5 %, 10 % and 20 %), see Figure 3-Right, the weight percentages of CO_2 captured, was respectively 4.1%, 4.2 % and 4.5 %, an increase in the concentration of the adsorbate in the gas flow favors the equilibrium, shift towards CO_2 capture.

Table 3: Percentage of captured CO_2 mass (wt %) by thermogravimetry in first and second cycle.

Sample	CO_2 (wt %) Cycle 1	CO_2 (wt %) Cycle 2	Sample	CO_2 (wt %) Cycle 1	CO_2 (wt %) Cycle 2
SBA-15	0	0	MCM-41	0	0
SBA-15(4)	4.3	4.2	MCM-41(7.5)	4.2	4.0
PEI-SBA-15(40)	4.7	4.5	PEI-MCM-41(60)	1.9	1.8

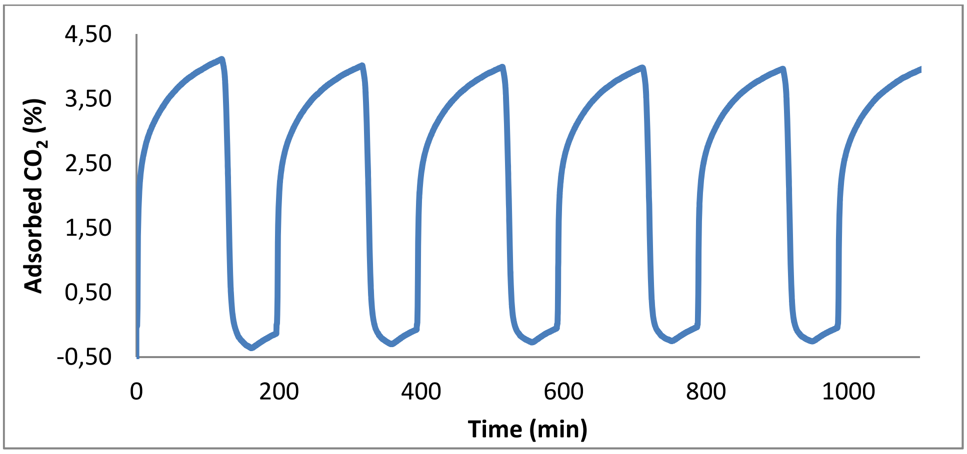

Figure 4: Isothermal (298K) CO_2 capture-regeneration cycle six times of MCM-41(7.5).

4. Conclusions

The materials amino-functionalization, by grafted with aminoxilanes and by impregnation with polyethylenimine, decrease drastically their mesoporous volume and specific surface area, which is the factor responsible for CO_2 physisorption. But the contribution of chemisorption associated to the incorporated amino groups improved the performance of the materials.

SBA-15 impregnated materials with polyethylenimine present higher levels of adsorption than MCM-41 impregnated materials. This is due to the SBA-15 larger pore size, while the small pore size of MCM-41 causes the polymer blocked pores, with lower percentages of polymer incorporated.

In the grafted MCM-41 materials, yield CO_2 capture is associated with the amount of aminoxilanes grafted material surface, whereas in the grafted SBA-15 samples, due to excessive addition of aminoxilanes with a sharp drop in the surface, CO_2 capture maximum occurs in materials with less incorporation of organic matter.

Amino-functionalized materials maintain a complete regeneration in the capture-regeneration cycles processes, in the six tested cycles.

CO_2 captures are slightly increased when the CO_2 concentration in the gas flow is increased (5 % -20 %) due to a displacement of the equilibrium towards CO_2 capture, when the partial CO_2 pressure increases.

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