TEMPERATURE EFFECT ON CO_2 ADSORPTION-DESORPTION PROCESS OF DIFFERENT FUNCTIONALIZED MESOPOROUS MATERIALS

Silvana Borcanescu, Alexandru Popa, Orsina Verdes, Mariana Suba

"Coriolan Drăgulescu" Institute of Chemistry, Blvd. Mihai Viteazul no. 24
300223 Timișoara, Romania,
e-mail: silvana.borcănescu@gmail.com

Abstract

In this paper was studied the adsorption-desorption of CO_2 and the effect of temperature on amino-functionalized mesoporous materials by using temperature programmed desorption – TPD method. The adsorption of CO_2 and its TPD method was investigated using thermogravimetric analysis coupled with a Pfeiffer-Vacuum-Thermo Star mass spectrometer. For this purpose MCM-41, SBA-15 and SSBA-15 functionalized mesoporous materials were prepared and investigated at different adsorption-desorption temperatures: 50, 60, 70 and 80°C. These composites were also characterized from the structural point of view: FT-IR spectroscopy and nitrogen physisorption at 77K.

Introduction

Mesoporous molecular sieves have been used as adsorbents, catalysts support, and heterogeneous catalysts in various applications [1, 2]. MCM-41 has great properties like uniform hexagonal cylindrical pore system, tunable pore size (15-100 Å), high surface area (>700 m^2/g), large pore volume ($\geq$0.7 cm^3/g), large number of silanol groups (~40–60%), negligible pore blocking effect, high surface reactivity and good hydrothermal, chemical and mechanical stability [3,4]. Due to investigations from previous years SBA-15 like MCM-41, presents also interesting properties like large surface areas (600–1000 m2/g), well-defined pore structure with variable pore diameters (50-300 Å) [5] and a highly ordered hexagonal mesostructure.

Modifying these materials with different organic groups (thiol, vinyl, amine, phenyl, propyl) has attracted much attention in recent years [6, 7]. Supported amine functionalized mesoporous silica presents a very great interest for CO_2 capture process due to very high selectivity towards CO_2 at low partial pressure, wide range of temperature [8, 9], adjustable uniform pore size, and facile surface functionalization schemes available [10, 11].

These materials have recently emerged as a promising class of solid adsorbents that can effectively adsorb CO_2 and regenerated using variety of approaches [12]. The present study was carried out to see how the temperature influences CO_2 adsorption-desorption process on these amino functionalized materials.

Experimental

Preparation of molecular sieves

MCM41 and SBA15 molecular sieves were tested from the adsorption-desorption point of view using TPD method. These molecular sieves were prepared by grafting, using 3-aminopropyl triethoxy silane as functionalization agent. MCM41 and SBA15 were functionalized by 3-aminopropyl-triethoxysilane. In a typical reaction, 1g of MCM41 or SBA15 was added in 50 mL toluene and the mixture was stirred for an hour. After that an excess of 3.39 mmol of $(C_2H_5O)_3Si(CH_2)_3NH_2$ was added and refluxed overnight. The white solid was removed from solvent by filtration washed with toluene and water and finally dried for 8 h under reduced pressure at 70 °C. A different sample named SSBA15 was prepared by the hydrolysis of tetraethyl orthosilicate using as surfactant a P123 block copolymer and 1-

phenyldecane as swelling agent. The synthesis of SSBA15: 4.6 g of Pluronic P123 was dissolved in 145 mL of HCl solution and stirred at 40 °C until the solution became clear. Then, 9.0 g of 1-phenyl-decane was added to the solution with stirring at 40 °C for 1 h. Finally, 0.05 g of NH_4F was added under stirring, followed by 9.0 g of TEOS. The above mixture was stirred at 40 °C for 24 h and then transferred to an autoclave for further reaction at 100 °C for 48 h.

The difference between the synthesis of SSBA15 and the synthesis of SBA15 is the presence of 1-phenyl-decane used as swelling agent. Modified SSBA15 was functionalized first by a silane coupling agent 3-glycidyl-oxypropyl-trimethoxysilane and finally by an amination reagent: ethylene diamine (N_2). The role of the amine used was to improve the CO_2 adsorption performance.

Methods

The resulted composites were characterized by thermal analysis using TGA/SDTA 851-LF 1100 Mettler apparatus. The thermal analysis system was coupled with a Pfeiffer—Vacuum—Thermo Star mass spectrometer by silica capillary at temperature of 200 °C. Adsorption measurements were carried out using the same thermogravimetric analyzer connected to a gas delivery manifold. High-purity CO_2 and 30%CO_2 in N_2 at 1 atm. was used for the adsorption runs, and N_2 was used as a regenerating purge gas for CO_2 desorption. In a typical adsorption –desorption run, a blank test of the empty sample container was performed at 25 °C in N_2 stream with a flow rate of 50 mL min^{-1} . Afterwards, the sample are weighed and placed in the sample container. The samples with mass of about 20 mg were placed in alumina crucible of 150 μL. The measurements were performed in dynamic air atmosphere with the flow rate of 50 mL min-1, in the temperature range of 25–650 °C with a heating rate of 10 °C min-1. Each sample was first pretreated in flowing N_2 at 150 °C, then cooled to the desired adsorption temperature (50-60-70-80°C), and exposed to 30% CO_2/N_2 (70 mL/min-1) for 120 min. The CO_2 adsorption capacity of the adsorbent in milligrams of CO_2 per gram of adsorbent was calculated from the mass gain of the sample in the adsorption process.

The FTIR absorption spectra were obtained with: Jasco 430 spectrometer in the 4000 - 400 cm^{-1} range, using KBr pellets.

The results in case of textural characteristics of the outgassed samples were obtained using Nova 2000 Quantachrome instrument series, N_2(g) adssorption-desorption technique.

Results and discussion

Infrared spectroscopy

The FTIR spectra of each sample were recorded and confirmed that SBA15 sil was successfully functionalized with ethylene diamine (not shown). The typical band of stretching vibration of Si-O-Si group in the silica structure appears at 1080, 800 and 461 cm^{-1}. The broad absorption band centered around 3440 cm^{-1} and a weak absorption band at 1630 cm^{-1} indicates the presence of water due to the absorbed water molecules in the sample, and belongs to the bending vibrations of H-O-H .The present bands at 1636–1522 cm^{-1} on the IR spectra of SSBA15sil+N2 were assigned to N–H stretching vibrations and N–H bending vibrations, respectively, providing evidence of the successful grafting of ethylene diamine onto SSBA15sil.

Specific surface area

The pore parameters of amino-functionalized molecular are listed in Table 1. The data reveal that the surface areas of MCM41 and SBA15 decreased after modification with 3-aminopropyltriethoxy silane (SBA15 sil and MCM41 sil samples). The reductions in surface areas can be attributed to the increase in agglomeration of silica particles and/or occupation of pores after modification.

Table 1. Textural properties of the studied composites

No.	Sample	Specific surface area (m^2/g)	Pore volume BJH$_{Des}$ (cc/g)	Average pore diameter BJH$_{Des}$ (nm)
1.	SBA15	725.0	1.19	6.64
2.	SBA15 sil	288.8	0.664	6.63
3.	SSBA15	766.5	1.294	6.62
4.	SSBA15 sil +N2	224.8	0.337	5.49
5.	MCM41	1299.7	0.695	3.30
6.	MCM41 sil	655.8	0.611	3.25

Thermal analysis

From thermal analysis in case of SSBA15 sil+N_2 the endothermic effect at 64 °C corresponds to the removal of small amounts of physically adsorbed water (Figure 2.). The mass loss represented by the peaks at 248 °C and 301 °C is due to the oxidation and the decomposition of amino propyl functional groups meaning that this material could be used for adsorption of CO_2 at temperatures below 250 °C.

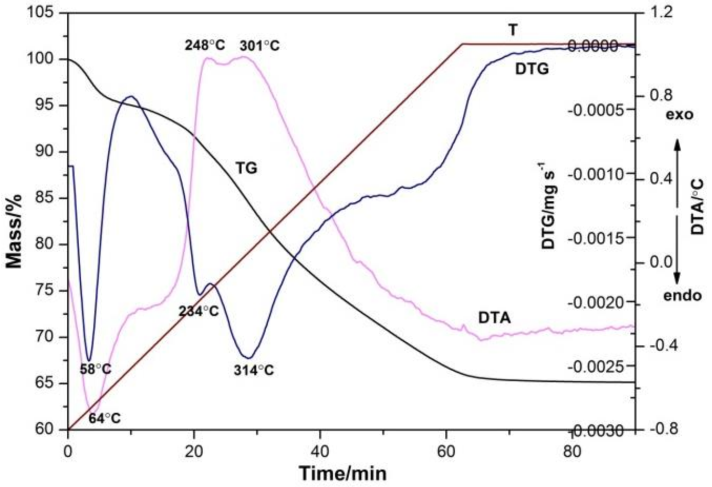
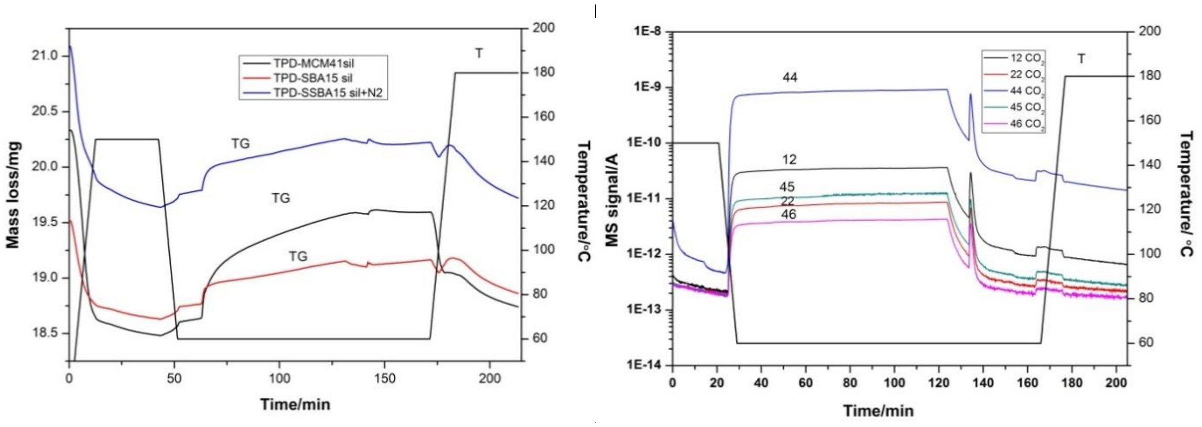


Figure 2. TG-DTG-DTA curves of SSBA15 sil + N2 composite.

For a possible use of these amino-functionalized molecular sieves as sorbents for CO_2 removal, their adsorption–desorption properties towards CO_2 were also investigated by TPD method. The adsorption-desorption of CO_2 and its TPD method using thermogravimetry were studied for amino-functionalized molecular sieves (Figure 3.)



a) b)

Figure 3. CO_2 adsorption-desorption steps of functionalized composites with isotherms at 60 °C (a) and MS analysis spectra of MCM41 sil at 60 °C(b).

Table 2. The amounts of the captured CO_2 on molecular sieves at different temperatures.

No.	Sample	n_{CO_2}/g SiO_2/mmol/g SiO_2			
		50°C	60°C	70°C	80°C
1.	MCM41sil	3.01	3.32	2.18	2.88
2.	SBA15 sil	0.86	1.23	1.09	0.79
3.	SSBA15 sil+N2	1.77	1.96	1.73	0.16

The CO_2 adsorption capacity of the adsorbent in mmol of CO_2 per gram of adsorbent could be seen from the mass gain of the sample in the adsorption process (Figure 3a) and was calculated more accurate from the mass loss during the desorption step. In Table 2, the amounts of the captured CO_2 on the composites are shown. The best result was obtained with MCM41 sil and SSBA15 sil+N2 samples and the optimal temperature for CO_2 adsorption–desorption by TPD results to be 60 °C.

The evolved gases during the adsorption–desorption of CO_2 on amino-functionalized molecular sieves were identified by online mass spectrometry coupled with thermogravimetry. As expected, the main compound observed in the evolved gases on MS spectra of amino-functionalized molecular sieves is CO_2 (Figure 3b).

Conclusion

In this paper was investigated the temperature influence over adsorption-desorption of CO_2 on amino-functionalized mesoporous materials using TPD method.

CO_2 adsorption–desorption of functionalized samples was studied for samples temperature ranging between 50-80 °C. The best result was obtained with MCM41 sil and SBA15sil+N2 composites and the optimal temperature for CO_2 adsorption–desorption by TPD results to be 60 °C.

The mass loss of SSBA15 sil+N2 above 250 °C is due to the decomposition of amino propyl functional group. This means that these amino-functionalized mesoporous materials are thermally stable below this temperature and can be used as sorbents for CO_2 as resulted from the mass spectroscopy.

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