EFFECT OF DIFFERENT SWELLING AGENTS ON TEXTURAL AND STRUCTURAL PROPERTIES OF MODIFIED MESOPOROUS SILICA

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Abstract

In this study was carried out the preparation of some large-pore ordered mesoporous silicas using a proper surfactant with different swelling agents. In order to use a micelle swelling agent with a moderate swelling ability we selected three swelling agents: 1-phenyl-decane, butyl benzene and mesitylene. The aim of these synthesis was to achieve a pore diameter enlargement but in the same time to avoid the formation of heterogeneous and/or poorly defined nanostructure of silica.

These composites were characterized by FT-IR spectroscopy, X-ray diffraction at low angles, nitrogen physisorption at 77 K, SEM-EDS. In the view of a possible use of these amino-functionalized mesoporous silicas as adsorbents for CO_2 removal, their adsorption–desorption properties towards CO_2 were investigated by the TPD method.

CO_2 adsorption isotherms of amino-functionalized mesoporous silicas measured at 50, 60 and 70 °C showed that the adsorption capacity (mg CO_2/g adsorbent) depend on the temperature of adsorption and on the type of swelling agents and amination reagents used.

Introduction

Solid sorbents adsorption is considered as a potential option for the CO_2 capture process. In the literature adsorption of CO_2 was investigated over a wide range of conditions on a series of mesoporous silica adsorbents comprised of conventional silica, MCM-41 and SBA-15 molecular sieves [1-3].

L. Bakhtiari et al. was shown that the use of swelling agent was an effective technique to control the pore characteristics in the mesoporous particles. The results showed that the use of an optimum amount of 1-dodecanethiol (swelling agent) can increase the pore diameter size and the distance between the pore centers [4].

So, the synthesis of mesoporous materials with amine functionalized groups with high adsorption capacity and selectivity for CO_2 capture process is an important task for the future.

Three different modified mesoporous silica compounds were synthesized by the hydrolysis of tetraethyl orthosilicate using as surfactant a P123 block copolymer and 3 different compounds as swelling agents: 1-phenyl-decane, butyl benzene and mesitylene. The prepared compounds were denoted as: SSBA-15-Dec, SSBA-15-BB and SSBA-15-Mes.

These composites were characterized by FT-IR spectroscopy, X-ray diffraction at low angles, nitrogen physisorption at 77 K, SEM-EDS and evaluated by the adsorption of CO_2 and its temperature programmed desorption – TPD.

Experimental

Three different modified mesoporous silica compounds were synthesized by the hydrolysis of tetraethyl orthosilicate using as surfactant a P123 block copolymer and 3 different compounds as swelling agents: 1-phenyl-decane, butyl benzene and mesitylene. The prepared compounds were denoted as: SSBA-15-Dec, SSBA-15-BB and SSBA-15-Mes.

For the synthesis of SSBA-15-Dec: 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 preparation method was almost the same for SSBA-15-BB and SSBA-15-Mes with the difference of swelling agent which was butyl benzene and mesitylene, respectively. After filtration and drying, the absorbents were obtained as white solids.

Textural characteristics of the outgassed samples were obtained from nitrogen physisorption at 77K using a Quantachrome instrument, Nova 2000 series instrument. The specific surface area S_{BET}, mean cylindrical pore diameters d_p and adsorption pore volume V_{pN2} were determined. Powder X-ray diffraction data were obtained with a XD 8 Advanced Bruker diffractometer using the Cu Kα radiation in the range $2\theta = 0.5 \div 5°$ and $2\theta = 5 \div 60°$. The FTIR absorption spectra were obtained with: Jasco 430 spectrometer in the 4000 - 400 cm^{-1} range, using KBr pellets. Microstructural characterization by SEM-EDS of the composites particles was carried out with a Jeol JSM 6460 LV instrument equipped with an EDS analyzer.

Adsorption measurements of CO_2 were carried out using a thermogravimetric analyzer TGA/SDTA 851-LF 1100 Mettler apparatus. High-purity CO_2 and 50% CO_2 in N_2 at 1 atm was used for the adsorption runs. Each sample was pretreated in flowing N_2 at 150 °C for 30 min, then cooled to the desired adsorption temperature and exposed to CO_2 for 120 min. Temperature programmed desorption (TPD) was performed by heating the sample from adsorption temperature to 180 °C with 10 °C/min and held at 180 °C for 30 min in N_2 flow 50 ml/min to regenerate the sorbent. The CO_2 adsorption capacity of the adsorbent in milimole of CO_2 per gram of adsorbent was calculated from the mass gain of the sample in the adsorption process.

Results and discussion

From N_2 adsorption-desorption isotherms (not shown) of parent samples (SSBA-15-Dec, SSBA-15-BB and SSBA-15-Mes) and grafted ones it could be concluded that all samples have a typical IV type of adsorption isotherms and a H1 type hysteresis loop, meaning that all materials have an orderly mesoporous pore structure.

Table 1 Textural properties of molecular sieves SBA-15 and modified mesoporous silica SSBA-15

No.	Sample	Specific surface area (m^2/g)	Pore volume BJH_{Des} (cc/g)	Average pore diameter BJH_{Des} (nm)
1	SBA-15	725	1.19	6.2
2	SSBA-15-Dec	766.5	1.29	6.62
3	SSBA-15-BB	579.8	1.30	9.81
4	SSBA-15-Mes	655.1	1.44	9.73

The effect of swelling agent could be observed for all textural properties (Table 1). For all 3 composites the specific surface area has close values and comparative with parent SBA-15 values, but the pore volume of prepared composites is larger than for parent SBA-15. The

average pore diameter for SSBA-15-BB and SSBA-15-Mes was around 10 nm, which was larger than the pore size of conventional rope-like SBA-15 (6.2 nm).

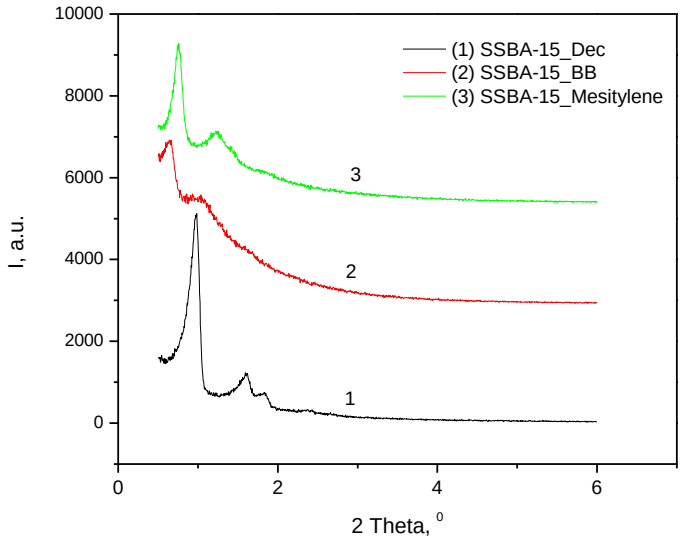

Fig. 1 XRD spectra of SSBA-15 with 3 different swelling agents: 1-phenyl-decane (a), butyl benzene (b) and mesitylene (c).

Figure 1 shows XRD patterns at low angles of the SSBA-15 samples prepared with 3 different swelling agents. As seen in this figure, SSBA-15-Dec sample show three well-resolved typical diffraction peaks, which are associated with a bi-dimensional p6mm hexagonal symmetry of the pores of classical SBA-15: one intense reflection centered at 0.87° and two lower intensity peaks at about 1.45° and 1.68°, which can be indexed as the (100), (110) and (200) hkl reflections, respectively.

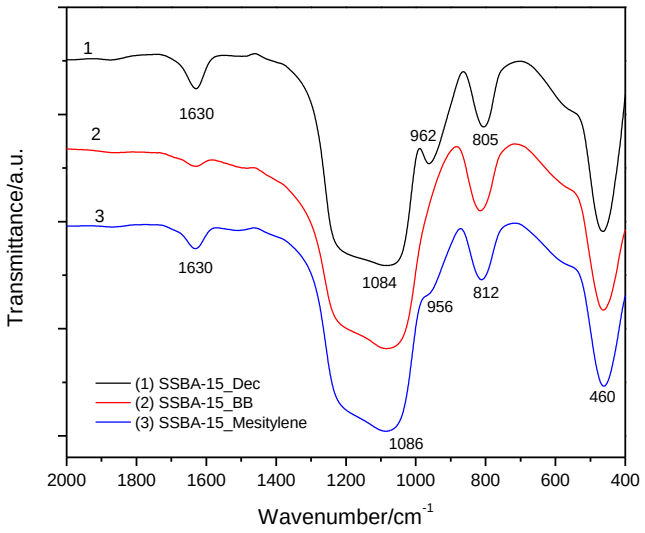

Fig. 2 Infrared spectra of SSBA-15 with 3 different swelling agents: 1-phenyl-decane (a), butyl benzene (b) and mesitylene (c).

SSBA-15-BB (0.64, 0.82) and SSBA-15-Mes (0.76, 1.24) have only 2 well resolved peaks which are shifted to lower angles by comparing with SSBA-15-Dec sample. The main

diffraction peak corresponding to (100) reflection is shifted to 0.64° for SSBA-15-BB , while for SSBA-15-Mes this peak is shifted to 0.76°.

All modified mesoporous silica prepared with 3 different swelling agents SSBA-15-Dec, SSBA-15-BB and SSBA-15-Mes showed that the characteristic IR bands of silica are evidenced by the three strong absorption bands at 1086, 810 and 460 cm-1 (Fig. 2). The IR bands at 1086 cm^{-1} belong to the anti-symmetric vibrations ν_{as} (Si–O–Si) and at 810 cm^{-1} to the symmetrical ν_s (Si–O–Si) bond. The IR bands 460 and 962 cm^{-1} have been assigned to the bending vibration of the bond δ (Si–O–Si) and the vibration of the silanol's group (Si–OH), respectively.

SEM images (Fig. 3 a-c) showed the changes of surface morphology on these obtained SSBA-15 particles in function of different swelling agents. Structural morphology of SSBA-15 modified with 1-phenyl-decane as swelling agent showed particles with long range well-ordered which have close aspect with conventional rope-like SBA-15. In fact, from textural analysis was evidenced that textural parameters of SSBA-15-Dec have values close to conventional SBA-15.

In contrast, the surface morphology of SSBA-15-BB and SSBA-15-Mes is different from SSBA-15-Dec and were consisted of cuboid-like particles. Also, from the values of textural parameters of modified SSBA-15 could be seen that SSBA-15-BB and SSBA-15-Mes have lower values of surface area but larger pore size than conventional SBA-15 and SSBA-15-Dec.

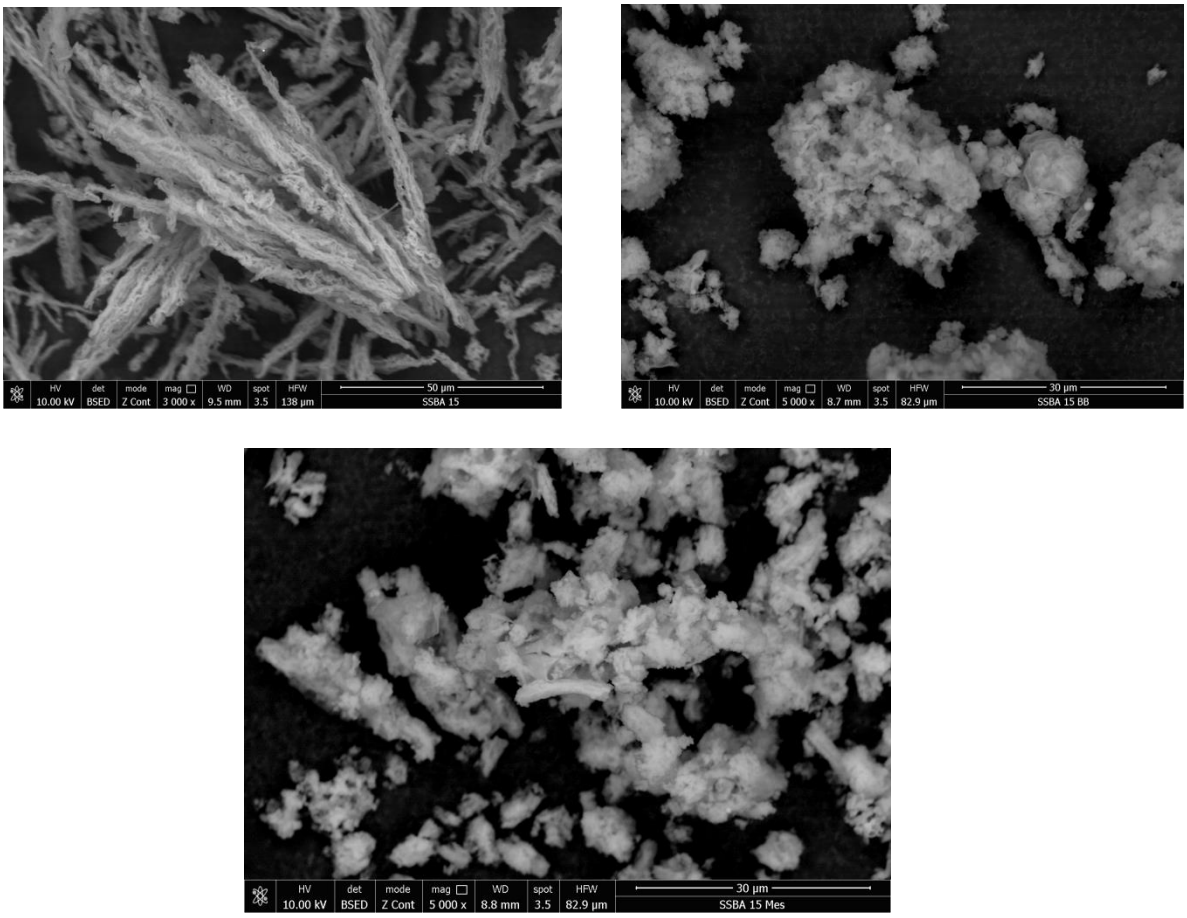

Fig. 3 SSBA-15 prepared with 3 different swelling agents: 1-phenyl-decane (a), butyl benzene (b) and mesitylene (c).

The adsorption of CO_2 and its TPD using thermogravimetry were studied for amino-functionalized molecular sieves. As we mention in experimental part each sample was pre-treated in flowing N_2 at 150 °C, then cooled to the desired adsorption temperature (50, 60 and 70 °C), and exposed to 50% CO_2/N_2 (70 ml/min) for 120 min. The desorption step was run in the range started from adsorption temperature until 180 °C with an increasing temperature rate of 10°C/min and with a isotherm at 180 °C for 30 minutes.

Table 3. The amounts of the captured CO_2 on molecular sieves at different temperatures.

No.	**Sample**	n_{CO_2}**/g SiO_2 [mmol/g]**		
		50°C	**60°C**	**70°C**
1.	SSBA-15-Dec-sil	2.24	1.94	1.54
2.	SSBA-15-BB-sil	2.82	2.89	2.28
3.	SSBA-15-Mes-sil	3.58	3.12	2.45

The CO_2 adsorption capacity of the adsorbent in mmole of CO_2 per gram of adsorbent could be seen from the mass gain of the sample in the adsorption process and was calculated more accurate from the mass loss during the desorption step. In Table 3 is shown the amounts of the captured CO_2 on all SSBA15 adsorbents. The best results were obtained with SSBA-15 - Mes-sil sample for the adsorption capacity of CO_2 at 50°C (3.6 mmole CO_2/g SiO_2) and at 60°C (3.1 mmole CO_2/ g SiO_2).

Conclusion

Three different modified mesoporous silica compounds were synthesized by the hydrolysis of tetraethyl orthosilicate using as surfactant a P123 block copolymer and 3 different compounds as swelling agents (1-phenyl-decane, butyl benzene and mesitylene) in order to achieve a pore diameter enlargement of silica.

From the values of textural parameters of modified SSBA-15 could be seen that SSBA-15-BB and SSBA-15-Mes have lower values of surface area but larger pore size than conventional SBA-15 and SSBA-15-Dec.

From the amounts of the captured CO_2 on all SSBA15 adsorbents by TPD, the best results were obtained with SSBA-15 - Mes-sil sample at 50° and at 60°C .

Acknowledgements

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References

[1] Cao L, Man T, Kruk M, Synthesis of Ultra-Large-Pore SBA-15 Silica with Two-Dimensional Hexagonal Structure Using Triisopropylbenzene As Micelle Expander. Chem Mater. 21 (2009) 1144.

[2] Kruk M, Cao L, Pore Size Tailoring in Large-Pore SBA-15 Silica Synthesized in the Presence of Hexane. Langmuir. 23 (2007) 7247.

[3] Popa A, Sasca V, Verdes O, Ianasi C, Suba M, Barvinschi P, Effect of the amine type on thermal stability of modified mesoporous silica used for CO_2 adsorption, J Therm Anal Calorim. 134 (2018) 269.

[4] Bakhtiari L, Javadpour J, Rezaie H R, Erfan M, Shokrgozar M A, The effect of swelling agent on the pore characteristics of mesoporous hydroxyapatite nanoparticles, Prog Nat Sci-Mater. 25 (2015) 185.