

## Capture of carbon dioxide by mesoporous carbon-silica composites

N. Stoeva\*, I. Spassova, D. Kovacheva, G. Atanasova, M. Khristova

*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences,  
1113 Sofia, Bulgaria.*

Received October 10, 2016; Revised November 11, 2016

Mesostructured silica-carbon composites were synthesized by soft template approach and were characterized by TG, XRD, low temperature N<sub>2</sub>- adsorption, TEM, XPS. The CO<sub>2</sub> adsorption capacities were investigated and the heats of adsorption were determined. The CO<sub>2</sub> capture from flue gas was tested. The carbon-containing materials exhibit better performance as sorbents for carbon dioxide than the single silica. For the silica-carbon composites improved CO<sub>2</sub> capture with increasing the carbon content is observed. The capacity of the silica-carbon materials for CO<sub>2</sub> capture from flue gas is related to the value of the average pore diameter of the composites and their micropore volume.

**Keywords:** silica-carbon composites; mesoporous adsorbents; CO<sub>2</sub> capture;

### INTRODUCTION

Fossil fuels as non-renewable resources are the major source of energy. Their burning produces billions tons of CO<sub>2</sub> and thus leads to severely adverse impacts on the environment, like air pollution and global warming. Therefore, the development of efficient low-cost way for reduction of CO<sub>2</sub> emission becomes important to control it. Currently, a variety of methods, such as membrane separation, cryogenic distillation, chemical absorption and adsorption, have been proposed for CO<sub>2</sub> purification from the flue gases [1]. Adsorption is considered as one of the most promising technologies for commercial and industrial application because of the low energy requirement, cost advantage, and ease of applicability over a relatively wide range of temperatures and pressures [2]. However, the success of this approach is dependent on the development of effective adsorbent with high CO<sub>2</sub> selectivity and adsorption capacity. During the past few years, extensive experimental and theoretical investigations were carried out with the purpose of developing novel porous materials for adsorption of CO<sub>2</sub> including zeolites, MOFs, mesoporous silicas and carbons [3-6]. Mesoporous materials are attractive for adsorption of gases due to the high specific surface area and relatively controllable porosity, moreover the rate of diffusion of CO<sub>2</sub> inside the pores of such adsorbents is ~ three orders

higher than with the liquid phase absorption. Carbon adsorbents are widely used for CO<sub>2</sub> capture due to their accessibility, low cost and low sensitivity to moisture. For the stabilization of mesoporous carbons siliceous materials could be used, as silica could serve as template material for the synthesis. Studies on mesoporous sorbents have shown that not only the pore volumes determine the sorption activity, but the pore sizes also [7]. These parameters can be adjusted during the synthesis of silica-carbon composites varying the ratio between silica and carbon.

Because of its relevance to practical applications, we found it compelling to synthesize mesostructured silica-carbon nanocomposites with various silica:carbon ratio in order to tune the texture parameters of the materials, to characterize them and to investigate the adsorption of CO<sub>2</sub> and the CO<sub>2</sub> capture from flue gas at higher than ambient temperature.

### EXPERIMENTAL

Mesostructured silica-carbon composites with a various Si:C ratio were prepared by co-assembly [8] of resol, silica oligomers from TEOS, and triblock copolymer Pluronic F127 via the EISA method. The thermal treatment was performed in two steps- at 350°C for 2h and at 900°C for 3 h. Single mesostructured silica and carbon samples were prepared by the same approach for comparison. Silica was treated at 550°C in air in order to remove the remaining carbon. Samples are denoted as MS (mesoporous silica), MSC1, MSC3,

\*To whom all correspondence should be sent:  
E-mail: n.stoeva@svr.igic.bas.bg

MSC5, MSC7 (with 10 % to 70% carbon) and MC (mesoporous carbon).

Physicochemical parameters of the composites were determined by TGA, XRD, N<sub>2</sub>-physisorption, TEM and XPS analyses. The TG analyses were carried out on LABSYSEvo, SETARAM (France) at atmospheric pressure in air in 25-1000°C and dynamic mode. Powder XRD patterns were collected on Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation and LynxEye detector. Low-angle part of the patterns was collected from 0.3 to 8° 2 $\theta$  using the knife-edge anti-scatter screen attachment of the primary beam. The texture characteristics were determined in a Quantachrome Instruments NOVA 1200e (USA). Pore size distributions were calculated by DFT method [9]. The TEM investigations were performed on a JEOL JEM-2100. The XPS measurements were made on ESCALAB-Mk II (VG Scientific) electron spectrometer with a Al K $\alpha_{1,2}$  radiation (h $\nu$  = 1486.6 eV).

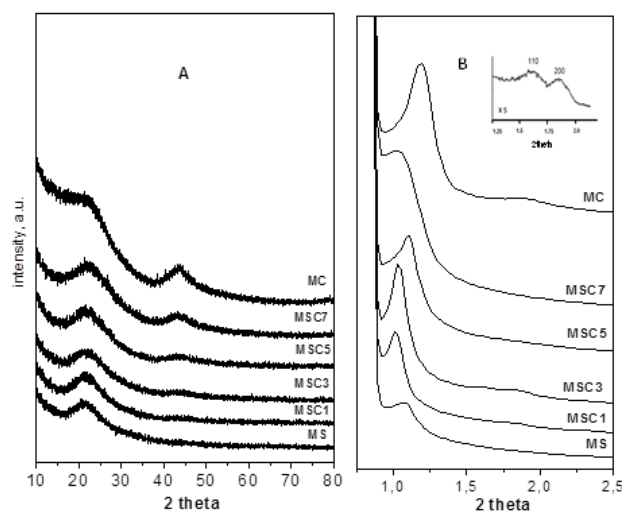
The adsorption isotherms and kinetics of CO<sub>2</sub> were measured using a static volumetric Quantachrome NOVA 1200e instrument. Isotherms were obtained at two temperatures (0°C and 30°C) for the purpose of determining heats of adsorption. The CO<sub>2</sub> capture experiments were performed using an integrated quartz micro-reactor and mass-spectrometer system (CATLAB, Hiden Analytical, UK). The CO<sub>2</sub> capture tests were performed at 45°C, with a concentration of 3000 ppm CO<sub>2</sub> in Ar, volume rate of 10 ml/min. The CO<sub>2</sub> uptake was calculated after integration of the curves and according to the exact weight of the sample.

## RESULTS AND DISCUSSION

The framework compositions were established by TGA. TG curves (not presented) show a significant weight loss for all samples in the temperature range from 500 to 1000°C, the range depending on the carbon content. The template is removed at about 350°C and the weight loss in 500-

900°C can be attributed to carbon. The obtained silica and carbon content is presented in Table 1 as SiO<sub>2</sub> and C.

XRD patterns of the samples are presented in Fig. 1. Wide angle pattern comprise of weak diffraction shoulder at 22.5° 2 $\theta$  due to the presence of amorphous silica (and or carbon) and a broad peak at 43.5° 2 $\theta$ , the intensity of the second one increases with the increase of carbon content (Fig. 1A), revealing formation of amorphous carbon in the composites. Low-angle diffraction patterns show two or three resolved diffraction peaks, indicating the well regularity of their structures in the long-range (Fig. 1B). The first intense diffraction peak can be indexed as (100). Because of the low intensity of the other two weak peaks in the diffractograms, (110) and (200) reflections are presented as inset with higher magnification. These peaks reveal a 2D-hexagonal symmetry (space group *p6mm*). The corresponding unit cell parameters  $a_0$ , calculated by the formula  $a_0=2d_{(100)}/\sqrt{3}$  are listed in Table 1. The unit cell parameter varies for the different compositions, single materials having the lowest values (Table 1).



**Fig. 1.** Wide-angle (A) and low-angle (B) XRD patterns of the investigated samples.

**Table 1.** Physicochemical and texture parameters of the synthesized samples.

Sample	$a_0$ nm $\pm 0.1$	SiO <sub>2</sub> (wt.%) $\pm 1$	C (wt.%) $\pm 1$	S m <sup>2</sup> /g	$S_{mi}$ m <sup>2</sup> /g	$S_{ext}$ m <sup>2</sup> /g	$V_t^*$ cm <sup>3</sup> /g	$V_{mi}^{**}$ cm <sup>3</sup> /g	$V_{mes}$ cm <sup>3</sup> /g	$D_{DFT}$ nm
MS	11.4	100	0	152	9	143	0.22	0.00	0.22	5.7
MSC1	12.1	84	16	206	19	187	0.29	0.01	0.28	4.8
MSC3	12.2	70	30	339	69	270	0.43	0.03	0.40	5.0
MSC5	11.2	53	47	387	49	338	0.53	0.02	0.51	5.1
MSC7	12.2	30	70	500	197	303	0.45	0.09	0.37	5.9
MC	10.3	0	100	588	223	365	0.36	0.10	0.27	4.5

\*Total pore volume at  $p/p_0 \sim 0.99$ . \*\*Evaluated by the t-plot method.

The errors of the determination of the texture parameters vary from 0.2 to 2% depending on the pressure and C-constant of the sample

The texture parameters of the materials are summarized in Table 1. With the increase of the carbon content specific surface areas and micropore volumes enlarge gradually, the total pore volume passes through maximum. Nitrogen adsorption-desorption isotherms (not presented) of all samples are of IV type with a distinct capillary condensation step occurring at  $p/p_0$  of 0.5–0.7. The pore distributions are narrow that is characteristic for the mesostructured materials. MS has the narrowest distribution and the addition of carbon leads to gradual broadening of the distributions due to the mesostructure framework shrinkage. Additional structural characterization is revealed by TEM images, as shown in Fig. 2. The images show large domains of highly ordered stripe-like well-ordered materials with arrays of mesopores with 1D channels. The pore width could be estimated from the images as varying from 5 nm to 7 nm, confirming the results from  $N_2$  physisorption. However, more detailed explanation could be done after HRTEM investigations.

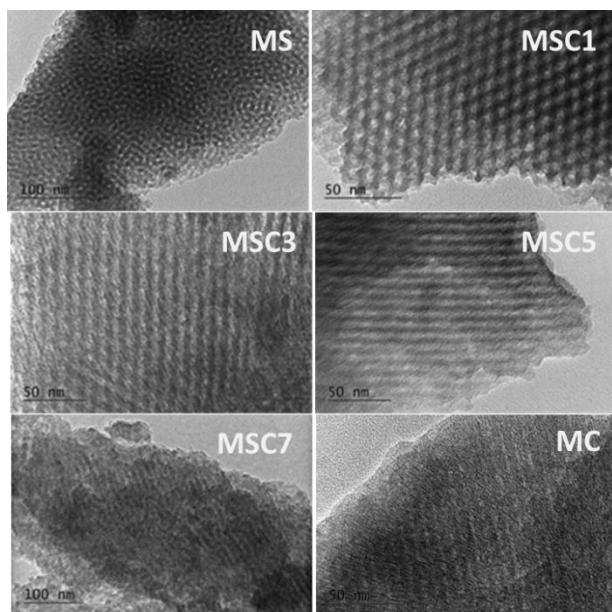


Fig. 2. Bright field TEM micrographs for the synthesized mesostructured materials.

Table 2. Surface composition

Sample	C [at.%]	O [at.%]	Si [at.%]
MS	6.7	56.3	37.0
MSC1	27.7	46.4	25.9
MSC3	42.0	35.4	22.6
MSC5	56.4	29.5	14.1
MSC7	80.8	13.4	5.8
MC	94.9	5.1	-

The corresponding surface composition of C, O and Si in all samples derived from the respective photoelectron peak area is presented in Table 2. Irrespective of the C and Si content (Table 1) in all cases the C content on the surface is higher than in the bulk. Hence, carbon in the composites is situated mostly on the external surface along the pores.

The adsorption isotherms of  $CO_2$  at 0°C and 30°C and pressure up to 100 kPa are given in Fig. 3. All isotherms have reversibility without hysteresis, indicating that the adsorbed gas molecules can be completely removed during the desorption. The isotherms have modest curvatures that suggest good regenerability of the adsorbent. Adsorption capacity is one of the major properties of the adsorbent. The  $CO_2$  uptake capacities at 100 kPa and at 0°C and 30°C are 4.0 and 2.9 mmol/g, respectively for MC. These values decrease gradually with increasing the silica content. The results are in a good agreement with the values obtained in [13].

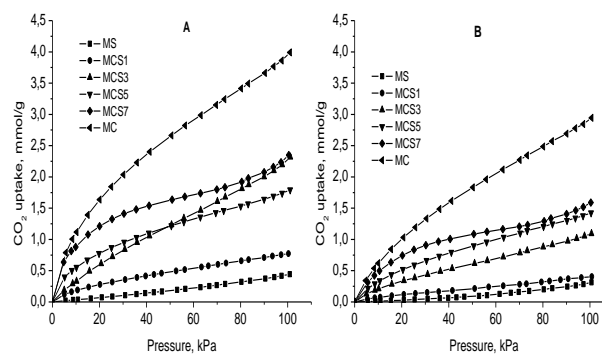


Fig. 3.  $CO_2$  adsorption isotherms at: A – 0 °C and B – 30 °C for various mesoporous silica-carbon composites.

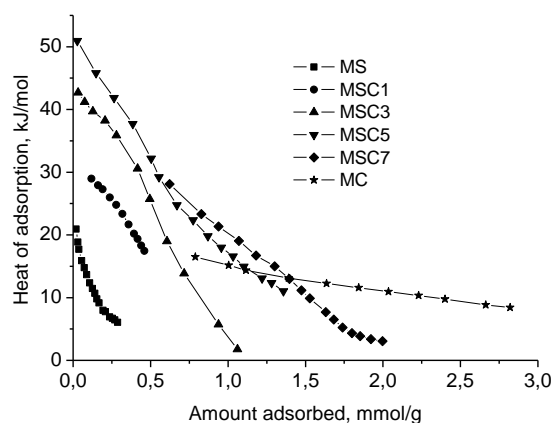


Fig. 4. Heats of adsorption for  $CO_2$ .

The heat of adsorption is always taken into account to estimate the temperature change of the adsorption process. On other hand, it is an indicator for the regenerability of the adsorbent and for the surface energetic heterogeneity of the material. The heats of adsorption (Fig. 4) decrease as the surface coverage increases within the experimental range, which can be attributed to decrease in the interaction between the adsorbate molecules and the surface with increasing loading. This indicates the heterogeneity of the surface for the adsorption of CO<sub>2</sub>. The limiting heats of adsorption at zero loading are calculated. Single MC and MS have lower values than mixed silica-carbon composites, however small change is observed with MC with increasing the surface coverage. At loadings greater than a monolayer the composites MSC5, MSC7, MC have larger adsorption heats than others.

The prepared silica-carbon composites as well as silica and carbon analogues were tested for CO<sub>2</sub> capture from flue gas in order to find whether these materials are suitable for purification.

Fig. 5 shows the CO<sub>2</sub> capture curves. Here, C<sub>0</sub> is the initial concentration of carbon dioxide and C is the concentration of CO<sub>2</sub> after time t.

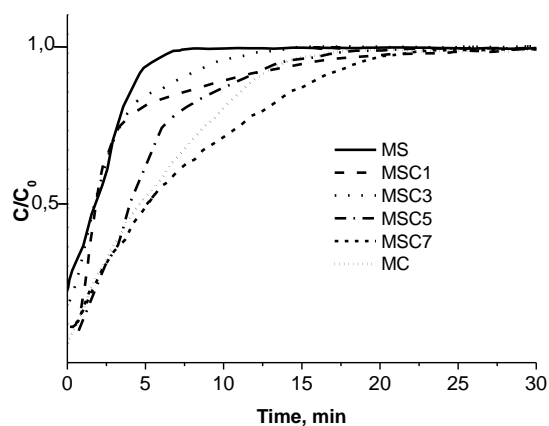


Fig. 5. CO<sub>2</sub> capture curves (0.3 vol% CO<sub>2</sub>, 10 ml/min, 45°C).

The CO<sub>2</sub> captures are found to be: MS- 3.2 μmol/g, MSC1- 3.5 μmol/g, MSC3- 4.3 μmol/g, MSC5- 5.9 μmol/g, MSC7- 9.7 μmol/g, MC-8.6 μmol/g. One could notice that the captured CO<sub>2</sub> quantity increases with increasing the carbon content in the composites. However, the pure carbon mesostructured MC presents less capacity than MSC7, showing the difference of the energetic state of the surface of the silica-carbon samples and the pure carbon. Apparently, the mixed samples ensure beneficial surface for the interaction with

CO<sub>2</sub>. This is in a good agreement with the heats of adsorption, presented in Fig. 4.

In generally, it is considered that large pore volume [14], large pore size [15], and good pore interconnection [16] is beneficial for the CO<sub>2</sub> capture capacity of sorbents. However, it was found that the values of the surface area and pore volume have little influence on the CO<sub>2</sub> capture performance of carbons [7]. Sevilla and Fuertes [17] have found that the CO<sub>2</sub> capture capacity seems to depend on the presence of narrow micropores rather than on the surface area or pore volumes. This is in a good agreement with our results, as the materials we found as the best samples have larger micropore volumes. Additionally, these materials are with large pore sizes, facilitating the mass transfer that is beneficial for CO<sub>2</sub> adsorption.

## CONCLUSIONS

The synthesized ordered mesoporous silica-carbon composites have high specific surface areas, uniform mesopore-size distribution, and large mesoporous volume. The CO<sub>2</sub> adsorption capture results indicate that the mixed materials exhibit better performance as sorbents for CO<sub>2</sub> than the single silica. The capacity of the best materials is related to the large average pore sizes and to the micropore volumes. Silica-carbon composites could be a good base for further chemical modification in order to improve the sorption capacity.

**Acknowledgements:** The authors gratefully appreciate the "Program for career development of young scientists, BAS" for the financial support (Project DFNP 197/14.05.2016).

## REFERENCES

1. K.M.K.Yu, I. Curcic, J. Gabriel, S.C.E. Tsang, *Chem. Sus. Chem.*, **1**, 893 (2008).
2. IEA Greenhouse Gas R&D Programme, CO<sub>2</sub> Capture and Storage, 2006.
3. G.-P. Hao, W.-C. Li, and A.-H. Lu, *J. Mater. Chem.*, **21**, 6447 (2011).
4. A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, **127**, 17998 (2005).
5. D. Zhao, Y. Wan, W. Zhou, *Ordered Mesoporous Materials*, Wiley-VCH, Weinheim, 2012.
6. S. Himeno, T. Komatsu, S. Fujita, *Adsorption*, **11**, 899 (2005).
7. L. Wang, M. Yao, X. Hu, G. Hu, J. Lu, M. Luo, M. Fan, *Appl. Surf. Sci.*, **324**, 286 (2015).
8. R. Liu, Y. Shi, Y. Wan, Y. Meng, F. Zhang, D. Gu, Z. Chen, B. Tu, D. Zhao, *J. Am. Chem. Soc.*, **128**, 11652 (2006).

9. A. Neimark, P. Ravikovitch, *Micropor. Mesopor. Mater.*, **44/45**, 697 (2001).
10. S. Gregg, K. Sing, Adsorption, Surface Area and Porosity, Second ed., Academic Press, London, 1982.
11. D. Chen, Z. Li, Y. Wan, X. Tu, Y. Shi, Z. Chen, W. Shen, C. Yu, B. Tu, D. Zhao, *J. Mater. Chem.*, **16**, 1511 (2006).
12. R. Ryoo, Ch. Ko, M. Kruk, V. Antochshuk, M. Jaroniec, *J. Phys. Chem. B*, **104**, 11465 (2000).
13. V. Saini, M. Andrade, M. Pinto, A. Carvalho, J. Pires, *Sep. Purif. Technol.*, **75**, 366 (2010).
14. X. Feng, G. Hu, X. Hu, G. Xie, Y. Xie, J. Lu, M. Luo, *Ind. Eng. Chem. Res.*, **52**, 4221 (2013).
15. X. Yan, L. Zhang, Y. Zhang, K. Qiao, Z. Yan, S. Komarneni, *Chem. Eng. J.*, **168**, 918 (2011).
16. C. Chen, S.-T. Yang, W.-S. Ahn, R. Ryoo, *Chem. Commun.*, 3627 (2009).
17. M. Sevilla, A. Fuertes, *J. Coll. Interface Sci.*, **366**, 147 (2012).

## УЛАВЯНЕ НА ВЪГЛЕРОДЕН ДИОКСИД ВЪРХУ МЕЗОПОРЕСТИ СИЛИКАТНО-ВЪГЛЕРОДНИ КОМПОЗИТИ

Н. Стоева, Ив. Спасова, Д. Ковачева, Г. Атанасова, М. Христова

*Институт по обща и неорганична химия, Българска академия на науките,  
1113 София, България.*

Постъпила на 10 октомври 2016 г.; коригирана на 11 ноември, 2016 г.

(Резюме)

Мезоструктурирани силикатно-въглеродни композити са синтезирани чрез мек темплейтен подход и са охарактеризирани посредством TG, XRD, азотна физисорбция, ТЕМ, XPS. Изследвани са адсорбционните капацитети спрямо CO<sub>2</sub> и са определени топлините на адсорбция. Тествано е улавянето на CO<sub>2</sub> от газов поток. Композитите, съдържащи въглерод показват по-добри резултати като сорбенти за CO<sub>2</sub> от чист SiO<sub>2</sub>. За силикатно-въглеродни композити се наблюдава подобро улавяне на CO<sub>2</sub> с увеличаване съдържанието на въглерод. Капацитетът на силикатно-въглеродни композити за улавяне на CO<sub>2</sub> от газов поток се свързва със средния диаметър на порите и с обема на микропорите .