

DE GRUYTER OPEN *MINERALOGIA*, 48, No 1-4: 47-62 (2017) DOI: 10.1515/mipo-2017-0011 www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND POLSKIE TOWARZYSTWO MINERALOGICZNE



Original paper

# Optimization of novel sorbents for CO<sub>2</sub> removal based on FTIR and TG analysis

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Received: April 30, 2017 Received in revised form: August 8, 2017 Accepted: August 26, 2017 Available online: September 30, 2017

Abstract. Adsorption is considered as one of the most promising technologies for CCS. Gas adsorption involves the separation of gaseous components from flue gas using solid adsorbents. The gaseous component, adsorbate, is adsorbed from the gas phase on a solid material. Regarding  $CO_2$  adsorption, it is important to consider the parameters, that is the high sorption capacity,  $CO_2$  selectivity, regeneration and stability in multiple cycles. New directions for the development of adsorbents are focused on increasing their capacity – for this purpose, amine impregnation is carried out. This paper presents a new approach to obtaining mesoporous material from fly ash and, based on this, a new physico-chemical adsorbent obtained by impregnation. The effectiveness of the process was confirmed by thermogravimetric analysis and FTIR infrared spectroscopy.

Key-words: CO2 adsorbent, FTIR, TGA, CO2 removal, CCS

### 1. Introduction

Nowadays, adsorption as a separation technique of  $CO_2$  is mainly used in postcombustion and oxy-combustion processes. Adsorbents have to fulfill the following criteria to be an effective material for  $CO_2$  removal from flue gas (Ho et al. 2008; Yang et al. 2012):

- high sorption capacity of CO<sub>2</sub>: 2-4 mmol CO<sub>2</sub>/g adsorbent;

- high surface area that favors more spots for CO<sub>2</sub> adsorption, which in turn is conducive to higher sorption capacity;
- fast kinetics of the process: the faster the adsorption kinetics, the faster CO<sub>2</sub> is adsorbed;
- high selectivity of CO<sub>2</sub>, which in addition contributes to higher purity of the CO<sub>2</sub> stream produced during desorption;
- smooth conditions regarding regeneration: when the parameter values (temperature and pressure) do not change rapidly, regeneration becomes cheaper;
- stability in adsorption/desorption cycles: the lifecycle of the adsorbent significantly affects the operating costs of the entire system;
- tolerance to pollutants (NO<sub>x</sub>, SO<sub>x</sub>, steam), as they can meaningfully affect the reduction of the adsorption capacity of CO<sub>2</sub>, and even adversely affect the crystalline structure of the adsorbent;
- flexibility in application, through which the adsorbent can adapt to different operating environments;
- low costs: due to their use, adsorbents are degraded and have to be replaced with new materials, hence it is important to maintain a minimal cost of exchange.

In the case of  $CO_2$  removal by adsorbents, it is important to gather information about the chemical composition, surface area, pore volume and pore size distribution, grain size density distribution, and the sorption characteristics: sorption capacities, and adsorption/desorption profiles, regeneration and lifecycle analysis. Adsorbents are tested in different research units; however, the optimization of their applications does not take into account the type of installations where the adsorbents will be used. Information can be found in the literature about the sorption capacities of CO<sub>2</sub> sorbents, mainly from their adsorption isotherms or the equilibrium capacity of CO<sub>2</sub> at a given temperature. Tests are usually conducted by using the thermogravimetric method in the case of the equilibrium capacity of CO<sub>2</sub>. Comparison of the research results obtained by thermogravimetric analysis is not easy, due to the differences in conducting research by various scientific units. Those differences are mainly caused by different conditions of conducting tests in accepted research procedures using TGA. The completed procedures were proposed elsewhere (Majchrzak et al. 2013; Majchrzak, Nowak 2017). Directions of the development of  $CO_2$  adsorbents are presented in Figure 1. The main purpose of this paper is to present the efficiency on modification with amine solid sorbents and to analyze CO<sub>2</sub> removal by using TGA thermogravimetric analysis and FTIR infrared spectral analysis. Regarding the above, synthesis and testing of the physico-chemical adsorbents (including those derived from fly ash from coal combustion) together with typical physical adsorbents were conducted. The assessment of the efficiency on the modification with the amine solid sorbents was carefully prepared. Effectiveness of impregnation was confirmed by TGA and FTIR studies.



Fig. 1. Directions of development of CO2 adsorbents

#### 2. Samples and methods

Experiments on the thermal stability and sorption characteristics were conducted by using a thermogravimetric analyzer (TGA/SDTA 851°). The obtained TG/DTG/SDTA curves were the result of the continuous registration of mass loss as a function of temperature. The sample was placed in a crucible on thermobalance. Next, it was heated under nitrogen or other gas mixture flows. The obtained TG curves were corrected by a blank test (TG curve of the corresponding inert sample, recorded in the given measurement conditions) in order to ensure the accuracy of the mass measurements. Another measurement by transmission method using pellets was carried out with an infrared FTIR spectrometer (Nicolet IS10). The pellets were prepared by grinding and rubbing in a mortar of approximately 1 mg of substance with 200 mg KBr. The sample weight ratio to KBr was 0.25%-0.5% and the area of the sample was approximately 1 cm<sup>2</sup>. Next, the sample was placed in a hydraulic press (tonnage capacity of the press equals 8 tons) with a pressure of 0.88 GPa. After removal, the pellet was placed into the measuring chamber of the FTIR spectrometer. The procedure proposed by Kumar et al. (2001) was used in order to obtain mesoporous material SBA-15 from the fly ash. According to it, surfactant tri-block copolymer (EO)<sub>20</sub>(PO)<sub>70</sub>(EO) dissolved in 2 mol/dm<sup>3</sup> HCl solution and sodium metasilicate were added to the Si filtrate in appropriate proportions, mixing the resulting reaction slurry at room temperature. Thirty-five percent HCl solution and water were added to the slurry. The obtained gel was kept for 1 day at room temperature, and then 3 days at 90°C. The resulting product was washed, dried and calcined at 550°C. For comparison of the result and effectiveness of using fly ash, synthesis of SBA-15 was also conducted by using chemically pure components, where the source of silica was tetraethyl orthosilicate (TEOS). Impregnation of the chosen materials was conducted according to the method of Xu et al. (2003). Accordingly, a suitable amount of amine was dissolved in 4 g of methyl alcohol and then stirred for approximately 15 min. The next step was to add 1 g of calcined physical adsorbent to the amine/methanol solution. The resulting mixture was shaken for 30 min and then dried at 70°C for 16 h at 700 mmHg. General information about the amines dedicated to impregnation is presented in Table 1. For the tests, the following physical adsorbents were chosen: activated carbons from coconut shells (AC from CECA Arkema Group and ORG from Desotec), carbon molecular sieve (MSC from Japan Takeda) and zeolite 4A (from Soda Polska Ciech). Impregnation with amines was performed on the adsorbents due to the acquisition of more adsorption sites for CO<sub>2</sub>.

	PEI Polyethyleneimine	DETA Diethylenetriamine	PEHA Pentaethylenehexamine
Summary formula	$(C_6H_{21}N_5)_n$	$C_4H_{13}N_3$	$C_{10}H_{28}N_6$
Molar mass, g/mol	750,00	103,77	232,37
Density, g/cm <sup>3</sup>	1,050	0,955	1,003

Types of amines used for the modification

#### 3. Results and discussion

Mesoporous material SBA-15 was synthesized from the fly ash (using silica and aluminum filtrate) and also by using chemically pure components, in order to compare the results and evaluate the effectiveness of using fly ash for synthesis. Fly ash was chosen from the PGE Opole power plant (Poland) regarding the amount of Si in the filtrate 6880 mg/dm<sup>3</sup>. Also, it was noted that the ratio of Si/Al was equal to 6.8. High content of Si in the original filtrate is important for good quality material. Figure 2 presents the XRD spectra of the calcinated material F-SBA-15 obtained from the fly ash. A peak of high intensity (100) can be observed, which confirmed the presence of a structure of SBA-15 in the obtained material. Diffractograms indicated that the filtrate from the fly ash from the PGE Opole power plant may be used in the synthesis of mesoporous material SBA-15. The isotherms (Fig. 3, 4) are type IV (according to IUPAC classification) with acute capillary condensation at  $p/p_0 0.35$  (Fig. 3) and 0.45 (Fig. 4), which confirmed the presence of mesoporous in the tested materials. In Table 2, the parameters of the porous structure of mesoporous material SBA-15 obtained both from the fly ash and the pure source of Si (TEOS) are presented. The F-SBA-15 showed lower surface area (303.1  $m^2/g$ ) relative to the SBA-15 (724.4  $m^2/g$ ), and also smaller volume and pore diameter.

TABLE 2

Parameters of porous structure of mesoporous material SBA-15 obtained from SBA-15 from filtrate of fly ash and pure source of Si (TEOS)

Sample	Surface area $S_{\text{BET}}$ , $m^2\!/g$	Pore volume, cm <sup>3</sup> /g	Diameter of pores, nm
F-SBA-15	303,1	0,22	3,3
SBA-15	724,4	0,79	4,3



Fig. 2. Diffractogram XRD of F-SBA-15 mesoporous material from fly ash

Modification of the mesoporous materials was carried out in order to introduce additional adsorption sites for  $CO_2$ . The impregnation method was proposed by Xu et al. (2003). Tests before and after modification were conducted in order to evaluate the influence of the PEI/PEHA/DETA amines on the structure of the modified adsorbents. The properties of the used amines and porous materials before and after the impregnation process were examined by analysis of the FTIR spectra and TG curves.



Fig. 3. Isotherm of adsorption/desorption of F-SBA-15 from fly ash



Fig. 4. Isotherm of adsorption/desorption of SBA-15 from chemically pure source of Si



Fig. 5. FTIR spectra of amines: PEI, PEHA and DETA

Figure 5 shows the spectra of the amines PEI, PEHA and DETA. During the tests, the branched PEI was used. It contains groups of primary, secondary and tertiary amines. Stretching vibration bands of N-H in the range from 3500 to 3200 cm<sup>-1</sup> can be observed for the primary amines- often two bands; secondary amines- one band; and tertiary- no band. On the spectra of liquid primary and secondary amines a hump can often be observed on the side of the lower frequency bands N-H, as a result of the overtone bands of enhanced bending vibration N-H from Fermi's resonance. The tertiary amines do not absorb in this range. Hence, in the obtained spectra no hump was observed. N-H bending vibration bands ('scissors' bands) appear for the primary amines in the range from 1650 to 1560 cm<sup>-1</sup>. For the secondary amines, bending vibration band N-H was observed at 1515 cm<sup>-1</sup>. The liquid samples of the primary and secondary amines show strong- or medium-width absorption bands in the range from 909 to 666  $\text{cm}^{-1}$  – these come from the fan noise of N-H. The location of these bands depends on the proportion of hydrogen bonds. C-N stretching is observed from 1342 to 1266 cm<sup>-1</sup> (Morrison, Boyd 1985; Silverstein et al. 2012). PEI, DETA and PEHA are one of the polyethylene amines. Figure 6 presents the FTIR spectra of the mesoporous materials F-SBA-15 before and after impregnation by using PEI (50wt.%).



Fig. 6. FTIR spectra of mesoporous materials F-SBA-15 before and after impregnation by using PEI (50wt.%)

The characteristic peaks at 1080 cm<sup>-1</sup> and 800 cm<sup>-1</sup> are the result of the asymmetrical and symmetrical vibration of SiO<sub>2</sub>, which is typical for mesoporous materials. The low intensity peaks associated with NH<sub>2</sub> (at 1600 cm<sup>-1</sup>) and CH<sub>2</sub> (at 1460 cm<sup>-1</sup>) are derived from the PEI used for impregnation and confirm its presence in the modified F-SBA-15 sample.

The peaks' characteristics for the group -C=O (at 1720 cm<sup>-1</sup>), -COO- (at 1550 cm<sup>-1</sup>) and -C-O (at 1250 cm<sup>-1</sup>) can be observed on the AC spectra (Figure 7). These bands are

associated with the carboxyl aromatic surface structures or conjugated chelate carboxylic structures and the C-O bonds. The peaks of the hydroxyl groups present on the surface and peaks associated with the occurrence of water chemisorption (4000-3450 cm<sup>-1</sup>) can also be read from the spectrum. After impregnation, on the FTIR spectra the bond related to the presence of N-H (at 1480 cm<sup>-1</sup>), the peaks at 1400 cm<sup>-1</sup>, 1677 cm<sup>-1</sup> and also the peaks' characteristics for the aliphatic chains at 2950 cm<sup>-1</sup> can be observed, which confirms the presence of amines. The spectra after modification were different from the original with lower intensity of bands.



Fig. 7. FTIR spectra of AC before and after impregnation by PEI, PEHA and DETA (50 wt.%)

Figure 8 presents the FTIR spectra of the carbon molecular sieve MSC before and after impregnation by PEI, PEHA and DETA (50wt.%). The observed bands are similar to those of AC. The characteristic bands for the carboxylic groups were observed at 1720 cm<sup>-1</sup>, 1550 cm<sup>-1</sup> and 1250 cm<sup>-1</sup>. Also, the peaks related to the hydroxyl groups present on the surface of the material and the peaks associated with the occurrence of water chemisorption can be read from the spectra in the range from 3450 to 4000 cm<sup>-1</sup>. Also, the spectrum after modification differs from the original with lower band intensity.

Figure 9 presents the FTIR spectra of zeolite 4A before and after impregnation by PEI, PEHA and DETA (50wt.%). The spectral bands show the presence of water from 3500 to 4000 cm<sup>-1</sup>. Similarly, the band characteristic for the H<sub>2</sub>O bonds occurs at 1640 cm<sup>-1</sup>. In the modified sample there is a low intensity peak from the amine used for impregnation at 1480 cm<sup>-1</sup>; correspondingly, there is a band characteristic for the aliphatic chains, which confirms the effectiveness of the modification of the adsorbents. The next step of the research was to careful investigate the influence of temperature on the adsorption process on the physical and physico-chemical adsorbents for CO<sub>2</sub> removal. Results were obtained

by using the developed procedure of the temperature programmed adsorption test (TPAT). The sample of sorbent (10 mg) was heated from approximately 25°C to 100°C in a nitrogen atmosphere (heating rate of 10°C/min) and maintained at this temperature for 15 min (until the constant mass of the sample established). The sample was then cooled to 25°C and the gas was switched to pure CO<sub>2</sub> and held there for a period of 2 h with the flow rate 50 ml/min. The increase in sorbent mass during this step was interpreted as the CO<sub>2</sub> sorption capacity at a given temperature. In the next step, the temperature increased at a rate of 0.25°C/min from 25°C to 100°C in order to determine the effect of temperature on the sorption capacity of the samples. The effect of temperature on the adsorption of  $CO_2$ was evaluated based on mass change during this stage. Then, the desorption process could be further carried out after conducting the process of sorption of CO<sub>2</sub>. Mass change during the running of the program made it possible to determine the temperature of the sorption capacity (and its change with temperature). The sorption capacity is given in mmol CO<sub>2</sub>/g adsorbent. Other procedures for the testing of adsorbent such as thermal stability, isothermal test for adsorption and desorption, or tests of multi-cyclic adsorption/desorption were described in detail elsewhere (Majchrzak, Majchrzak-Kucęba 2013; Majchrzak, Nowak 2017).



Fig. 8. FTIR spectra of MSC before and after impregnation by PEI, PEHA and DETA (50wt.%)



Fig. 9. FTIR spectra of zeolite 4A before and after impregnation by PEI, PEHA and DETA (50wt.%)



Fig. 10. Temperature programmed test of adsorption CO<sub>2</sub> (TPTA) on the 4 physical adsorbents AC, ORG, MSC and 4A, and also on the physico-chemical mesoporous material F-SBA-15 from fly ash impregnated by PEI: tests were conducted in an atmosphere of 100%vol. CO<sub>2</sub>, flow- 50ml/min. (1) isothermal adsorption profile at 25°C; (2) adsorption profiles as a result of TPTA

Figure 10 shows the results of the temperature programmed adsorption of CO<sub>2</sub> for the 4 physical adsorbents AC, ORG, MSC and 4A, and for the physico-chemical sorbent F-SBA-15 modified by PEI (F-SBA-15 PEI). It was observed that at 25°C, the sorption capacity of

F-SBA15-PEI was equal to 0.99 mmol  $CO_2/g$  adsorbent. This value is lower than those obtained at the same temperature on the physical sorbents (AC, ORG, MSC and 4A; Fig. 10.1). The sorption capacity of the physical sorbents is highest at 25°C and decreases rapidly as the temperature rises. This is the direct effect of the physical adsorption of CO<sub>2</sub> that occurs in this case. Physical sorption is strongly dependent on temperature: adsorption is an exothermic process, so the adsorption coefficient always decreases with increasing temperature. However, increases in the sorption capacity along with increases in temperature were observed in the physico-chemical adsorbent. This is due to the combination of physical adsorption derived from the initial sample and the chemical adsorption due to the presence of amine groups on the surface of the mesoporous material. It can be observed in Fig. 10.2 that at 90°C the adsorbent F-SBA15-PEI reaches the highest sorption capacity of 2.16 mmol CO<sub>2</sub>/g adsorbent. Presumably, this is related to the fact that as the temperature rises, the PEI becomes more flexible and more CO<sub>2</sub>-friendly sites are available. Hence, the sorption capacity increases. Also, it should be emphasized that chemisorption requires activation energy, which can be delivered thermally. According to the above fact,  $CO_2$  capacity increases because at higher temperatures the chemisorption is faster; as per physical sorption, chemisorption is also an exothermic process, so in the equilibrium state the capacity also decreases with temperature. At 90°C, the AC has a sorption capacity of 0.5 mmol  $CO_2/g$  adsorbent, which is 3 times lower than at 25°C. Zeolite 4A showed a smaller decrease in sorption capacity with increasing temperature, reaching 1.77 mmol CO<sub>2</sub>/g adsorbent at 90°C. The sorption capacity of physical adsorbents regarding CO<sub>2</sub> decreases with increasing temperature. This is related to the exothermic character of physical sorption, in which both the molecular diffusion coefficient and surface energy of the adsorption decreases with increasing temperature.

Figure 11 presents the results obtained during the desorption process by raising the temperature to 70°C, without rinsing the bed with nitrogen. Experiments were conducted using AC and AC modified with PEI. The results are presented using TG and DTG curves. Due to fact that desorption at 50°C results in incomplete desorption and raising the temperature to 70°C gives satisfactory results for a single cycle, it was decided to conduct adsorption at 30°C and desorption at 70°C, simulating Temperature Swing Adsorption (TSA) in the TG analyzer. Cycles were repeated 10 times to test the stability of the adsorbent. The length of a single cycle was 15 min for the adsorption and desorption, while the complete test lasted approximately 500 min (Fig. 11). The individual stages of regeneration were characterized by high stability. The sorption capacity in the first cycle was 1.27 mmol  $CO_2/g$  adsorbent, and the final (after the last cycle) was 1.14 mmol  $CO_2/g$ adsorbent. Reduction of the sorption capacity after 9 cycles was approximately 10%. In the case of the activated carbon AC, only increasing the temperature to 70°C (40°C more, relative to the sorption temperature) resulted in 100% regeneration (Fig. 11). Regarding the DTG curves, no sorption reduction on the AC over many cycles was observed. A similar situation occurred with the AC modified PEI, where there was also 100% regeneration at 70°C. Compared with the sorption/desorption curves of the AC and AC-PEI, the modified sorbents (AC PEI) show they need more time to reach equilibrium capacity, which confirms that impregnation slows down the kinetics of the sorption/desorption process of  $CO_2$ , probably due to the diffusion of  $CO_2$  by the amine layer. By observing the profile of



Fig. 11. Cyclic adsorption/desorption profiles of  $CO_2$  removal using activated carbons as adsorbents: AC (1) and AC PEI (2). Temperature of sorption 30°C, temperature of desorption 70°C

the desorption curve for the modified AC, it can be stated that it is different from the starting AC, indicating that the regeneration in this case is not complete (the share of chemisorption hinders regeneration). It follows that in the case of AC, impregnation is not advantageous because it drastically reduces the volume of micropores and decreases the sorption capacity. The original AC had a high specific surface area and high  $CO_2$  sorption capacity, and impregnation reduced the sorption capacity, which was a negative effect on this solid sorbent. Active carbon is therefore a good  $CO_2$  adsorbent without the need for modification, which in this case is not a good solution as PEI blocks the microporous AC texture that is primarily responsible for the physical sorption of  $CO_2$  to AC. The solution would be for such a modification to introduce the contribution of chemisorption, but without reducing the physical sorption. Figure 12 presents the profiles of the adsorption/desorption cycles on the physico-chemical adsorbent F-SBA-15 modified by

using PEI. Studies were carried out in three successive cycles of adsorption/desorption of  $CO_2$  at 90°C under the flow of 100%vol.  $CO_2$ . Repeated use of the sorbent does not cause a noticeable reduction in its sorbent capacity, which confirms good sorbent stability and its ability to be used in multi-cycle processes. The measurement line goes into negative values because in the case of regeneration by raising the temperature during the first cycle, equilibrium was reached in a shorter time than in subsequent cycles due to the longer time needed in the TGA system to cool again to room temperature after the first cycle. However, this status was reflected in subsequent cycles and does not affect the sorption capacity directly.



Fig. 12. TG profile of sorption/desorption of CO<sub>2</sub> on F-SBA-15 PEI in three successive adsorption/desorption cycles at 90°C, desorption under nitrogen, gas flow: 50ml/min

Excellent stability of the  $CO_2$  adsorbents over many cycles is very important in terms of the practical applicability of adsorbents described in many adsorption/desorption cycles. Similarly, Xu et al. (2003) and Xu et al. (2005), who conducted an experiment consisting of two continuous adsorption/desorption cycles, found that the adsorption of  $CO_2$  on PEImodified commercial mesoporous material MCM-41 decreased slightly in the next cycle. Therefore, regeneration is complete and adsorbent is stable throughout the entire  $CO_2$ capture process. Desorption of  $CO_2$  under appropriate conditions for the tested material was 100%. This stability is comparable to the result obtained for the amine-modified mesoporous material (KIT-6-PEI-50) in studies by Son et al. (2008). Adsorption/desorption profiles also showed that the desorption process is fast enough and that the  $CO_2$  is desorbed almost completely until the end of the experiment.

Sorption and desorption on  $CO_2$  solid adsorbent were also tested in the TG-FTIR system. The gas products released during the process were subjected to continuous detection using the TG-FTIR conjugated system. Tests were conducted for the physical adsorbent AC at the configuration of the adsorption/desorption at 25°C/25°C and for the AC modified with PEI at 75°C/75°C. Adsorption was carried out under 100%vol.  $CO_2$ . Desorption was carried out by flushing the bed with nitrogen. Gas flow was set at 50 ml/min. Full interpretation of the IR spectra is very difficult because there are many deformations and stretching vibrations around the particle. As a result, the recorded

spectrum contains many different bands that correspond to vibrations. Each of the different types of bonds has a similar energy difference between the oscillatory levels. They absorb radiation at a given characteristic frequency, resulting in the same bandwidth regardless of the other particle structure details. Therefore, most functional groups yield strongly characteristic bands and their position in the spectrum is comparable, for example C=O, N–H or O–H. This study attempted to perform analyses of the individual spectra obtained by conducting  $CO_2$  capture and adsorbent regeneration processes. The OMNIC program for the data analysis and creating graphs of the recorded measurements enabled the presentation of the selected FTIR spectra in 3D, as shown in Figure 13 and Figure 14.



Fig. 13. 3D FTIR spectra of AC on adsorption/desorption products; sorption temperature 25°C/desorption temperature 25°C, desorption under nitrogen flow



Fig. 14. 3D FTIR spectra of AC PEI on adsorption/desorption products; sorption temperature 25°C/desorption temperature 25°C, desorption under nitrogen flow

During the FTIR tests, Gram–Schmidt curves were obtained which allowed FTIR spectra to be obtained from the given moment of the adsorption/desorption experiment and a particular section of the graph to be selected in the OMNIC program. Spectral changes in the intensity of the individual absorption bands were recorded during the measurement. Through the processes of dehydration, adsorption and desorption the following emissions were observed:  $CO_2$  (1740-1700cm<sup>-1</sup>), N<sub>2</sub> (3300-3200 and 2250 cm<sup>-1</sup>) and also H<sub>2</sub>O (3850 and 1300-2000 cm<sup>-1</sup>).

#### 4. Conclusions

Synthesis and testing of physico-chemical adsorbents (including those derived from fly ash from coal combustion), together with typical physical adsorbents is an innovation in this paper. Efficiency of the modification with amine was evaluated for the physico-chemical sorbents, while the effectiveness of impregnation was confirmed by TGA thermogravimetric analysis and FTIR infrared spectral analysis. Amine modification was used in order to increase the maximum sorption capacity at higher temperature. However, research showed the effective modification was possible only with the mesoporous materials SBA-15. Impregnation on activated carbons, molecular carbon sieve and zeolite by selected amines did not produce any effects. The preferred results were only obtained for the mesoporous material from the fly ash F-SBA-15 using PEI. This new material can be identified as a physico-chemical sorbent. This is due to the fact that solid adsorbent (mesoporous material) adsorbs physically, whereas the chemical substance used for impregnation (amine PEI) adsorbs in a chemical manner. In summary, for the physico-chemical adsorbents (modified mesoporous material from fly ash), the following characteristics were found:

- high sorption capacity at temperature in the 70-90°C range makes physico-chemical sorbents more effective than physical materials, which exhibit lower sorption capacity at these temperatures;
- studies of adsorption/desorption cyclic processes showed total CO<sub>2</sub> desorption, which confirmed the reversibility of reaction and the ability to use sorbent in many cycles;
- easy regeneration (small difference between the temperature of adsorption and desorption);
- very high sorption capacity at low CO<sub>2</sub> concentrations: these sorbents are favorable for post-combustion technology, where CO<sub>2</sub> concentrations are approximately 10-15%vol. (as opposed to physical adsorbents);
- rapid desorption of CO<sub>2</sub> from PEI-impregnated mesoporous materials F-SBA-15 indicates very good dispersion of PEI in mesoporous structure, as demonstrated by TGA studies;
- small or no effect of vapor is characteristic for physico-chemical sorbents, which also distinguishes them from physical adsorbents.

Acknowledgements. This scientific work was supported by the National Centre for Research and Development, as Strategic Project PS/E/2/66420/10 "Advanced Technologies for Energy Generation: Oxy-combustion technology for PC and FBC boilers with CO<sub>2</sub> capture." The support is gratefully acknowledged.

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