

Studies on the CO₂ Adsorption onto Coal Fly Ash Zeolites at Elevated Pressures

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Abstract Coal fly ash zeolites (CFAZs) of Na-X type were prepared by ultrasonic-assisted double stage fusion-hydrothermal synthesis from lignite coal fly ash at two different fusion temperatures 550 and 800 °C. The detailed surface analyses were performed experimentally using N₂ physisorption technique and by applying standardized mathematical models. CFAZs were studied for their carbon capture potential at 5.5 MPa regarding their application in a pressure-swing CO₂ adsorption process. CO₂ loaded CFAZs were investigated by weight analyses, Fourier-Transform Infrared (FTIR) and Thermal Gravimetric Analyses (TGA). FTIR reveals vibration modes typical for the zeolite Na-X framework, physically attached CO₂ molecules and small amounts of carbonates. The adsorption capacity toward CO₂ measured by weight analyses and TGA reaches 385 mgCO₂/gCFAZ. Higher carbon capture ability was found at CFAZ prepared with a pre-fusion stage at 800 °C, despite its the lowest specific surface area. A favourable effect of the increased content of mesopores in the CFAZ framework on the CO₂ adsorption at elevated pressures has been established.

Keywords: Pressure-swing carbon capture, Low-carbon energy, Coal fly ash utilization

1. Introduction

Recently, coal fly ash zeolites (CFAZs) have provoked widespread scientific interest as CO₂ adsorbents with applicability in carbon capture and utilization technologies (Wee, 2013, Monasterio-Guillot, 2020). The development of efficient adsorbents for carbon capture by utilization of solid by-products from combustion processes will contribute to significant environmental and economic benefits (Czuma et al., 2020). It has been revealed in previous studies that CFAZs are regenerated with less energy consumption than natural and pure synthetic zeolites due to their mixed micro-mesoporous texture that facilitates mass transfer processes (Zgureva and Boycheva, 2020). For industrial applications of gas flow separation, drying and purification, adsorption by solids is broadly applied. The pressure-swing adsorption (PSA), at which the

adsorption mode is performed at elevated pressures, while the regeneration mode is accomplished by depressurizing is widely investigated and developed. PSA is preferable process when highly porous materials such as zeolites are used as adsorbents, as the amount of adsorbed gas increases with increasing pressure due to the effects of capillary condensation into the pores (Kim et al., 2014). PSA is also considered as a technologically feasible process for production of fuels by separation of hydrogen from CO₂/H₂ syngas or when catalytic chemisorptions is performed for CO₂ methanation (Moon et al. 2016). After the subsequent release of the synthetic gas fuel, it is directed for downstream utilization, storage or combustion. The present study is emphasized on the CO₂ retaining potential of CFAZs at elevated pressures and their suitability as adsorbents in PSA carbon capture systems.

2. Experimental

CFAZs were obtained by applying ultrasonic-assisted double stage alkaline conversion of lignite coal fly ash by a laboratory procedure described elsewhere (Boycheva et al., 2020). The sample denoted as CFAZ_1 was synthesized with a pre-fusion stage carried out at 550 °C, while CFAZ_2 and CFAZ_3 were obtained from reaction mixtures pre-fused at 800 °C. CFAZs were characterized regarding their surface parameters by N₂-physisorption using an adsorption analyzer TriStar II 3020, Micromeritics. The samples were preliminary heated up to 260 °C in continuous helium flow for releasing the accumulated in the pores atmospheric gaseous components. Specific surface area values (S_{BET}, m²/g) were calculated by applying Brunauer-Emmett-Teller (BET) model to the monolayer adsorption region of the experimental isotherms. The pore size distribution functions were examined by t-plot and Brunauer-Joyner-Halenda (BJH) computational models applied to the desorption isotherms. The high pressure adsorption was carried out in a stainless steel reactor Miniclave 100, Büchiglasuster. CFAZs in an amount of 0.2 g were packed in semi-permeable bags and exposed to pure CO₂ at a pressure of 5.5 MPa for

72 h. CFAZs were not pre-dried for technological convenience. CO₂ loaded samples were characterized by Fourier-transform infrared spectroscopy (FTIR) using a spectrometer Tensor 37, on standard KBr pellets. Thermogravimetric analyses (TGA) were performed in the thermal range 40-800 °C using an apparatus TGA-4000 Perkin Elmer at heating rate 8 °C/min up to 220 °C, and further at 10 °C/min.

3. Results and Discussion

The experimentally obtained N₂ adsorption/desorption isotherms are plotted on Fig. 1. All of the measured isotherms outline hysteresis loops and could be classified as type IV (IUPAC, 1985), which is typical for micro-mesoporous materials. The adsorption of N₂ molecules in monolayer for all samples was occurred at relative pressures up to $p/p_0=0.05$ in which the BET model was applied. Intensive adsorption in this pressure range is registered for the sample CFAZ_1 related to the significant presence of micropores. The progressive adsorption at higher p/p_0 range and the wider hysteresis loops at CFAZ_2 and CFAZ_3 are related to the increased content of meso- and macropores in the zeolite structure.

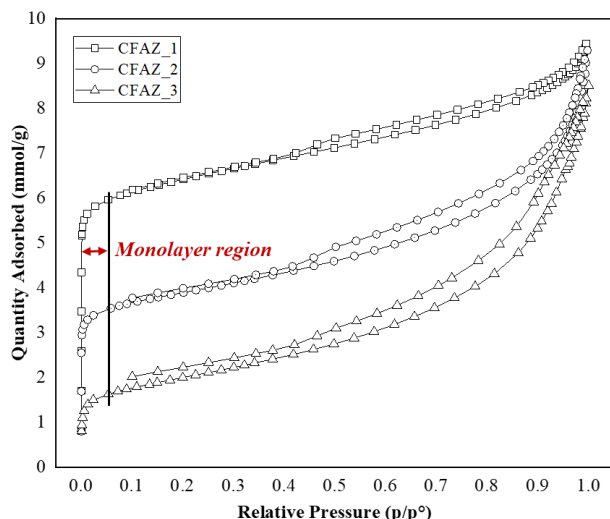


Fig.1. Experimental N₂-adsorption/desorption isotherms

CFAZs surface parameters calculated by the standardized models applied to the experimental N₂-adsorption/desorption isotherms are summarized in Table 1. Surface studies reveal lower specific surface area (S_{BET}) values for the samples obtained at the higher fusion temperature but a bigger share and larger diameter of the mesopores in their framework. BJH plots representing the distribution of the free volume by pore sizes are presented in Fig. 2. The plot for CFAZ_1 reveals a maximum volume fraction for pores below 30 Å in diameter. The distribution peak is shifted to larger pore diameters in the samples obtained at higher fusion temperatures. The BJH model is applicable for the mesoporous region, while precise calculations for microporosity were provided by applying density functional theory model (DFT). The predominant microporosity in CFAZ_1 was confirmed by DFT.

Table 1. Surface parameters of CFAZs.

Sample	S_{BET} , m ² /g	V_{total} , cm ³ /g	V_{micro} , cm ³ /g	V_{meso} , cm ³ /g	d_{micro} , Å	d_{meso} , Å
CFAZ_1	553	0.30	0.16	0.14	14	38
CFAZ_2	328	0.25	0.09	0.16	14	48
CFAZ_3	160	0.21	0.02	0.19	12	56

S_{BET} – specific surface area; V_{total} – total pore volume; V_{micro} and V_{meso} – pore volume described by micro- and mesopores.

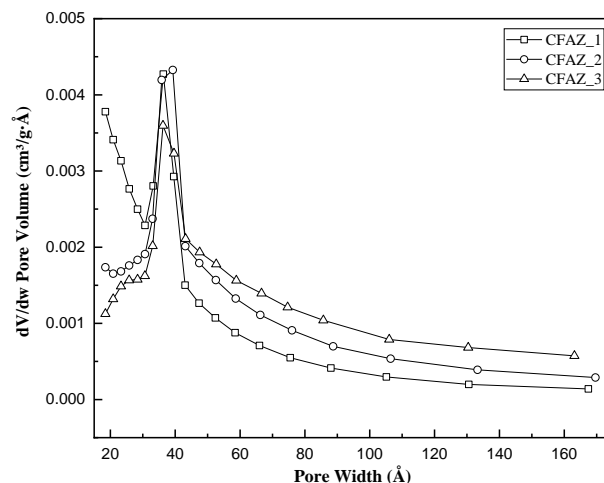


Fig. 2. BJH plots of the investigated samples

In the FTIR spectra of the all samples common features of vibrational modes typical for the structural framework of the zeolite Na-X (Karge, 2001) and for CO₂ molecules are observed. The assignments of the IR adsorption bands are summarized in Table 2. FTIR patterns evidence physical adsorption of CO₂ and formation of a small amount of carbonates (Fig. 3). The CO₂ load at 5.5 MPa on CFAZs measured by weight analyses is given in Table 3 together with the CO₂ adsorption capacity at 0.1 MPa calculated by fitting of the experimental isotherms measured at pressures up to 104.6 kPa to the Langmuir model, as it is demonstrated in Ref. (Zgureva and Boycheva, 2020). Langmuir adsorption model assumes monolayer adsorption onto uniformly distributed surface sites (Sircar, 2017).

Table 2. FTIR adsorption bands assignment

Vibration mode	Adsorption band, cm ⁻¹
OH-stretching vibrations	3458
Adsorbed H ₂ O molecules	1650
Internal asymmetric vibrations in the TO _{4/2} tetrahedra	986 1069
Symmetric Si-O stretch	668 752
Double six-rings vibrations	562
T-O bends	465
Asymmetric stretch vibration of carbonate group	1523 1418
Adsorbed CO ₂ molecules	2360 2338

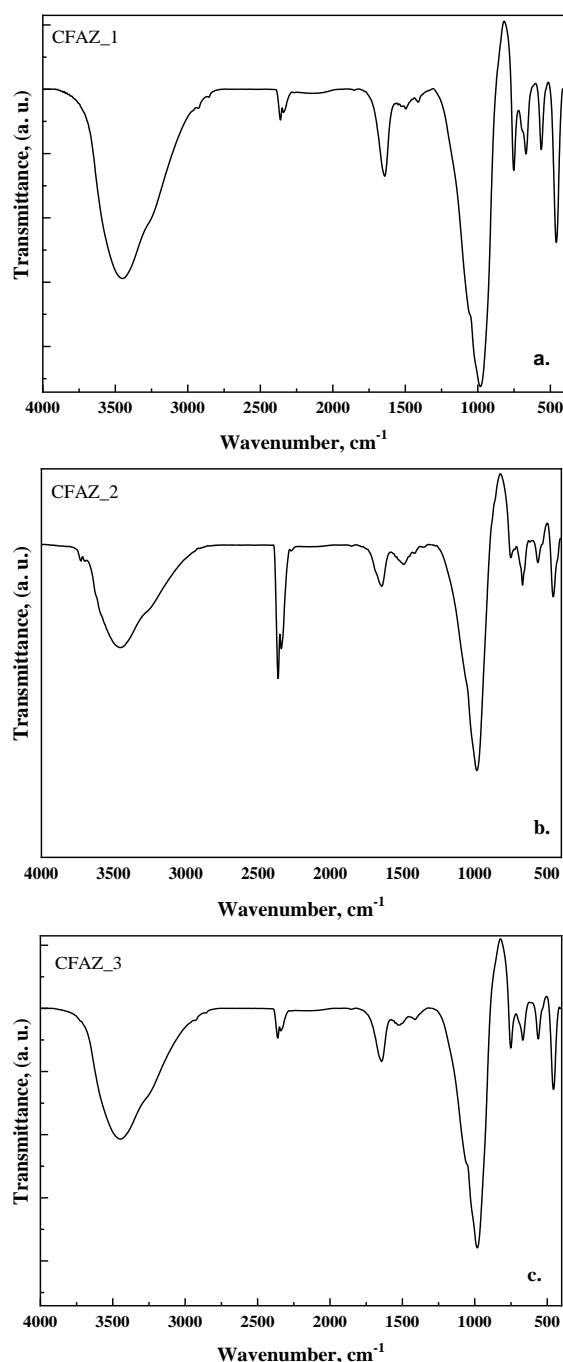


Fig.3. FTIR spectra of CO₂ loaded coal fly ash zeolites at 5.5 MPa.

Since the experimental measurements were made for non-dried samples, the results for CO₂ load were recalculated for dry mass based on the weight analysis of moisture content. Zeolite materials are characterized by a high retention capacity of water molecules in their porous structure and, in general, before their application as adsorbents, it is necessary to dry them in order to release their internal free volume. This is the main technological drawback in the application of zeolites as adsorbents, related to the increased energy demands for the pre-drying process. Reported studies reveal that the moisture content in gas streams up to 20 vol. % improves CO₂ capture by solid adsorbents (Younas et al, 2015). Our previous studies also confirm that the equal volume ratios of water and carbon dioxide in the treated gas do not impair the CO₂ adsorption onto

CFAZs (Boycheva et al., 2021). This provoked the study of the CO₂ adsorption under high pressures to be carried out without pre-drying of the samples. It was established a high ability of non-dried CFAZs to capture CO₂, which is a prerequisite for technological convenience of the carbon capture. The results on the CO₂ adsorption studies at elevated pressures reveal that the retaining capacity of CFAZs increases (Table 3), and this dependence is more pronounced in the samples with higher mesoporosity.

Table 3. CO₂ load onto CFAZs at 0.1 Pa and 5.5 MPa

Sample	5.5 MPa		0.1 MPa
	mg/g wet mass	mg/g dry mass	mg/g
CFAZ_1	154	183	155
CFAZ_2	300	330	117
CFAZ_3	385	404	141

Despite the broader specific surface area of CFAZ_1, the adsorption of CO₂ at elevated pressures is the lowest due to the narrowest average diameter of mesopores and the smallest internal free volume obeyed by the mesoporosity in the structure of the sample. In Fig. 4 are plotted the experimental TG-DTG curves of the CO₂ loaded samples. Measurements of weight losses during the heating were carried out in the temperature range 40-800 °C. A wide endothermic zone is registered at all studied samples at temperatures up to about 200 °C due to the release of moisture and CO₂. However, the measured mass losses from the TGA in this temperature range are lower than the cumulated moisture content and the adsorbed amount of CO₂ measured by the weight analysis. The reason for this is the instantaneous desorption of CO₂ molecules adsorbed on the external surface of the CFAZ particles after the samples taking out of the CO₂ ambient. In the case of adsorbents with high surface-to-volume ratio an accelerated desorption process is established at the end of their exposure to the test analyte, which favors their regeneration by reducing energy demands. When the temperature rises in the range of 50-100 °C, the CO₂ molecules retained in the pores of CFAZs are released. Small weight losses as a result of endothermic effect at about 700 °C due to the formation of calcium and/or magnesium carbonates were also registered, which is also confirmed by the FTIR analysis.

4. Conclusions

Coal fly ash zeolites obtained by ultrasonic-assisted double stage fusion-hydrothermal synthesis were studied for their carbon capture potential in a pressure-swing adsorption process at 5.5 MPa. It was found that the dominant factor for the high retention potential toward CO₂ at high pressures is the larger share of mesopores in the structure of the adsorbents, which can be achieved by managing the synthesis conditions. The highest measured CO₂ adsorption capacity reaches above 400 mg/gCFAZ. Ultrasonic-assisted synthesis of

adsorbents provides a high surface-to-volume ratio, which reduces the energy regeneration demands of adsorbents. It was found that the pressure-swing CO₂ capture is carried out mainly on physical adsorption mechanism accompanied by carbonization of the alkaline earth metals present in the coal fly ash zeolites. This is a prerequisite for the potential of the investigated materials to operate in multiple adsorption/regeneration cycles. The presence of water into the zeolite matrix does not interfere the CO₂ capture at elevated pressures. From practical point of view this is beneficial for post-combustion carbon capture from flue gases which usually contain a significant amount of water vapor.

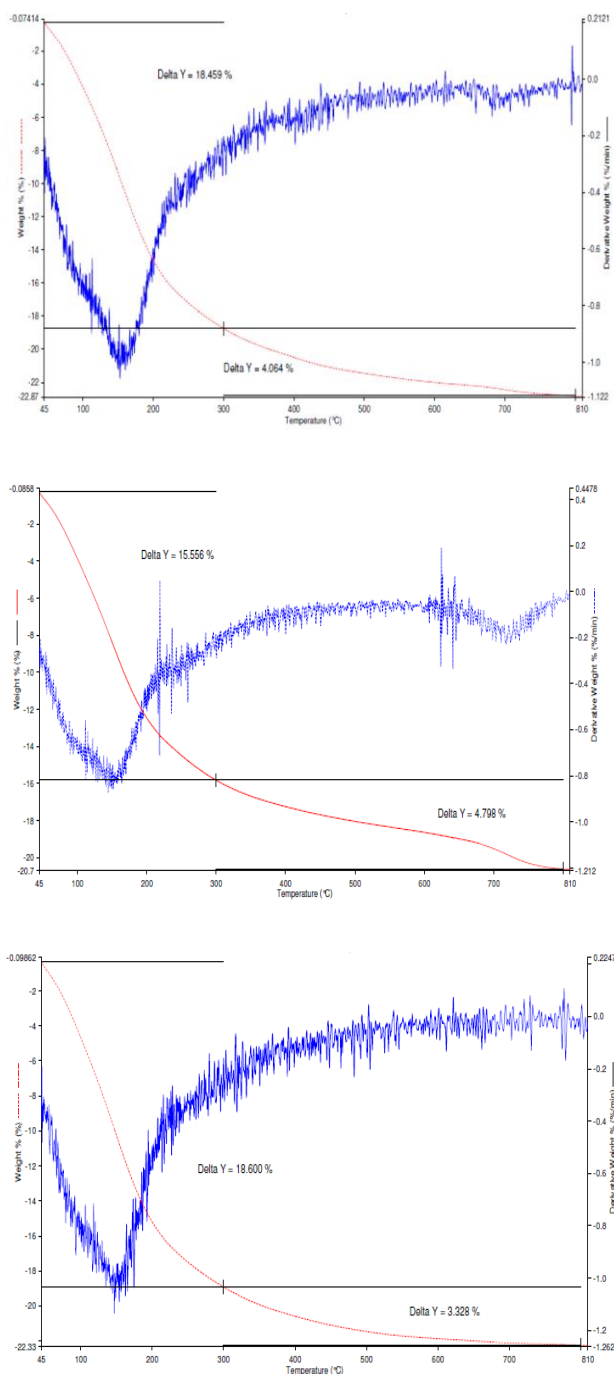


Fig. 4. Experimental TG-DTG plots of CO₂ loaded CFAZs.

Acknowledgements

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