Fly ash zeolites as a dual system for simultaneous CO$_2$ capture and its utilization in the production of synthetic gas

D M Zgureva$^1$, S V Boycheva$^2$ and K B Filipov$^2$

$^1$ College of Energy and Electronics, Technical University of Sofia, 8 Kliment Ohridski Blvd, Sofia, Bulgaria
$^2$ Department of Thermal and Nuclear Power Engineering, Technical University of Sofia, 8 Kliment Ohridski Blvd, Sofia, Bulgaria

E-mail: dzgureva@tu-sofia.bg

Abstract. The deepening of global environmental problems caused by carbon emissions (CO$_2$) generated by various industries requires the development of technological solutions to limit their emitting into the atmosphere. Electrical power plants that use organic fuels as a primary energy source are serious emitter of CO$_2$. The current legislation prerequisites the implementation of technologies for carbon capture and utilization (CCU - Carbon Capture and Utilization) situated at the plant site. In our previous studies, we successfully applied the zeolites synthesized from fly ash obtained from combustion of lignite coal as solid adsorbents for selective capture of CO$_2$ in equilibrium and dynamic conditions. The aim of this study is upgrading of the fly ash zeolite utilization in a dual system for simultaneous carbon capture and CO$_2$ utilization for production of synthetic gas. Experiments were performed in a stainless steel laboratory reactor Büchiglasuster Miniclave 100 in equilibrium conditions at CO$_2$ pressure of 0.25 MPa with different duration. The solid samples saturated with CO$_2$ and reaction products were extracted from the reactor and subjected to gravimetric analyses and Furier-transform infrared spectroscopy (FTIR). The characteristic vibrations of C$_{2}$H$_{2n+2}$ molecules were observed onto FTIR spectra of the samples after their exposure for long time.

1. Introduction
Simultaneously with the industrial peak and the development of technologies, the parameters of the environment are also changing, as for the last 50-60 years the International Energy Agency (IEA) reports more than a twofold increase in the generated carbon dioxide (CO$_2$) [1]. The higher concentration of CO$_2$ into the atmosphere is considered as a key factor influencing the deepening of global warming, which leads to rising ground surface temperatures [2]. The transport sector and the energy production have the biggest share as CO$_2$ emitters due to the oxidation of organic fuels during the combustion processes. The contribution of hydrocarbon fuels (coal, oil, and gas) as primary energy sources in the world gross electricity production for 2018 is 63.9 %, and the coal has the biggest share of 38 %. Because of the necessity of diversification in the energy sector, the complete abandonment of fossil fuels is not economically and technically feasible. This requires intensive development and research of technological solutions to reduce CO$_2$ emissions into the atmosphere from Thermal Power Plants (TPP). Two main approaches are simultaneously explored: Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU). The CCS is based on the capture and concentration of pure CO$_2$, followed by its liquefaction and transportation for storage in deep geological formations, which is associated with high expenses for real scale application. The CCU approach is suitable for
implementation on site of the TPP, and it proposes the utilization of pre-captured CO$_2$ in commercial products. For both technologies, the stage of CO$_2$ separation from the flue gas flows has been comprehensively investigated. It has been found that for the existing TPPs the process of physical adsorption is the most efficient from an economic and technical point of view [3-4]. In our previous studies, zeolites synthesized from fly ash obtained from combustion of lignite coal were successfully applied as solid adsorbents for selective capture of CO$_2$ in equilibrium and dynamic conditions [5-6].

Expanding the use of fly ash zeolite (FAZ) in the CCU system will be a cost-effective technological solution to overcome two environmental challenges for TPPs: huge amounts of fly ash waste disposal and greenhouse gas emissions. According to IEA statistical reports, only 0.15 Gt out of a total of 32.5 Gt CO$_2$ generated in 2017 are utilized in various sectors [1]. The direct use of CO$_2$ amounts to 20.10$^6$ tCO$_2$, with the share of food packaging production being 50 %, industrial gases 35 %, and carbonated beverages 15 %. The indirect use of CO$_2$ amounts to 130.10$^6$ tCO$_2$ for 2017 and is mainly due to its conversion into substances and raw materials, which is in most cases at the research stage. A promising CCU technology is the conversion of CO$_2$ into hydrocarbon fuels, and there are several research installations for the production of synthetic gas and oil that utilized 10.10$^3$ tCO$_2$ in 2017.

This study is a part of comprehensive scientific study devoted to the FAZ application in CCU for production of synthetic gas. The broad surface, specific micro-mesoporous structure of FAZ, the presence of intermetallic inclusions, and the high content of iron in two oxidation extents (Fe$^{2+}$ and Fe$^{3+}$) are prerequisites for enhanced ability of these materials to capture and catalyze the reaction of CO$_2$ with the silanol groups from the zeolitic framework for the production of C$_n$H$_{2n+2}$. Preliminary results show the potential of FAZ to act as a triple system adsorbent-carrier-catalyst at pressure of 5.5 MPa, which can be applied for both CO$_2$ capture and its catalytic conversion [7]. The aim of this study is to evaluate the potential of FAZ in low pressure hydrocarbonization to optimize the process parameters required to scale the laboratory experiment.

2. Materials and methods
The FAZ exposed to CO$_2$ were obtained by double-stage alkaline treatment of fly ash (FA) from lignite coal and coal mixtures combusted in TPPs. Three different FAs were used as raw materials and they were collected from the electrostatic precipitators of TPP AES Galabovo (FA$_{AES}$), TPP Dimitrovgrad (FA$_{DM}$) and iron-enriched separate from the filter’s bottom part (FA$_{Fe-S}$). The applied synthesis procedure was performed in a following consequence: a high temperature pre-fusion stage at 550 or 800 $^\circ$C of mixtures of 10 g FA and 5g NaOH used as an alkaline activator; crushing of the cooled agglomerate and dilution in 100 ml distilled water; ultrasonic homogenization of the reaction slurry for 15 minutes; hydrothermal activation stage was carried out at 90 $^\circ$C for 4 hours. The synthesized powder materials were extracted by filtration, washed and dried. The synthesis products were subjected to X-Ray diffraction analyses and Scanning electron microscopy for structure and morphology identification. It was observed that the resulting fly ash zeolites (FAZ) were characterized by a dominant faujasite structure (FAU), similar to that of commercial Na-X zeolite, and were composed of nanosized and submicron crystals. As a major factor determining the adsorption processes, the textural properties of the samples were also studied by N$_2$-physical adsorption technique. The standardized BET model was applied to the adsorption branch of isotherms in the region of monolayer adsorption (p/p$_0$=0.05-0.15) for the specific surface area calculation ($S_{BET}$, m$^2$/g). The volume of micropores ($V_{micro}$, cm$^3$/g) was calculated by t-plot modelling of adsorption isotherms, and the volume of mesopores ($V_{meso}$, cm$^3$/g) by applying of BJH equation to the desorption branch. The textural properties of all samples are summarized in table 1.

Experiments for CO$_2$ adsorption and its catalytic conversion in hydrocarbons were performed in a stainless steel laboratory reactor Büchiglasuster Miniclave 100 in equilibrium conditions at pressure of 0.25 MPa for 18 hours (Case 1) and 114 hours (Case 2). The initial weight of all samples was 0.2 g and after their exposure, the gravimetric analyses were performed by analytical scales with an accuracy of ±0.0002 g. The samples were also studied by Fourier transform infrared spectroscopy (FTIR) on a Brucker Tensor 37 apparatus to identify the CO$_2$ physisorption and chemisorptions products.
Table 1. Samples subjected to CO2 exposure.

| Sample  | Raw FA | Tf °C | S_BET m²/g | S_external m²/g | V_total cm³/g | V_micro cm³/g | V_meso cm³/g | d_micro Å |
|---------|--------|------|------------|----------------|--------------|--------------|--------------|-----------|
| Sample 1 | AES    | 550  | 334        | 109            | 0.2196       | 0.0894       | 0.1302       | 13.78     |
| Sample 2 | AES    | 800  | 404        | 113            | 0.2819       | 0.1058       | 0.1761       | 13.80     |
| Sample 3 | AES    | 800  | 160        | 118            | 0.2087       | 0.0182       | 0.1905       | 11.78     |
| Sample 4 | DM     | 550  | 421        | 108            | 0.3027       | 0.1234       | 0.1793       | 14.06     |
| Sample 5 | Fe-S   | 800  | 134        | 118            | 0.1432       | n/a          | 0.1432       | n/a       |

3. Results and discussions

The results from gravimetric analyses are shown in table 2, where δm in g is the change between the initial and final sample weight. The percentage increase in sample weight after exposure compared to baseline was given for the two case studies (table 2). In case 1, where the exposure time is shorter, a significant increase in the weight of the exposed samples is observed, which is indicative for the accumulation of CO2 into FAZ by physical adsorption or hemisorption. The intensive change of samples’ mass for Case 1 could be explained with physical or chemical reaction between CO2 and FAZ during the exposure. The captured amount of CO2 assuming physical adsorption is presented in table 2. The results for Samples 1, 3 and 4 correspond well to our preliminary investigations for equilibrium CO2 adsorption onto FAZ at a pressure range of 0.0001-0.1 MPa, described by the Langmuir model [5]. Sample 5 is characterized by the lowest value of the specific surface (table 1), but it shows the highest amount of captured CO2 (table 2). Since sample 5 has the highest content of iron oxide phases (hematite α-Fe2O3, magnetite γ-Fe2O4), it can be assumed that iron oxides contributed to additional hemisorption of CO2. A number of studies show that iron oxides have active sites exposed at the surface, which can react with the gaseous molecules of CO2, which leads to formation of siderite [8]. The CO2 capture of Sample 2 is unexpectedly low compared to the large specific surface area of this zeolite. Also, this value is significantly lower than that measured in the adsorption tests at equilibrium conditions at lower pressure. Our previous studies show that the FAZ obtained by the melting step at 800 °C and subsequent ultrasonic homogenization are characterized by a fine dispersion of the iron oxide phases in the zeolite matrix and a significant amount of ionic iron [9]. In these zeolites from coal ash, high catalytic activity has been found in oxidative processes. This leads us to assume that in Samples 2 and 3, the measured low value from the gravimetric analysis does not show a low potential for CO2 retention of these FAZs, but rather this result is due to catalytically stipulated CO2 conversion process. During the catalysis temporary complexes are formed, then they decompose and the catalyst is recovered which leads to the maintaining of constant total mass of the system. For all samples from Case 2 at which long exposure in CO2 ambient was performed, almost a slight change in mass is observed. To establish the transformation of CO2 in hydrocarbons onto the FAZ surface the FT-IR spectra were analyzed and they are plotted on figure 1.

Table 2. Results from gravimetric analyses of samples exposed to CO2 at 0.25 MPa.

| Sample  | Case 1 (τ=18 hours) | Case 2 (τ=144 hours) |
|---------|---------------------|----------------------|
|         | δm g                | Weight increase %    | δm g                | Weight increase % |
| Sample 1 | 0.0639               | 31.95                | 0.0008              | 0.40               |
| Sample 2 | 0.0247               | 12.35                | 0.0012              | 0.60               |
| Sample 3 | 0.0206               | 10.30                | 0.0008              | 0.40               |
| Sample 4 | 0.0735               | 36.75                | 0.0005              | 0.25               |
| Sample 5 | 0.1028               | 51.40                | 0.0007              | 0.35               |

In the low wavelength region (400-1100 cm⁻¹) could be observed the typical vibration for zeolite structures in different structural cages [10]. Non intensive peaks in this region for Sample 5 confirm
the lowest zeolitic yield established by XRD and surface analyses. The IR-spectra of the all samples reveal a wide adsorption band at 2800-3700 cm\(^{-1}\) where typical vibration for O-H group (3200-4000 cm\(^{-1}\)) and C-H bonds (2800-3200 cm\(^{-1}\)) are situated. Adsorption bands corresponding to C-O from physically adsorbed CO\(_2\) in region of 2100-2300 cm\(^{-1}\) and of 1500-1800 cm\(^{-1}\) are observed in the IR-spectra for the all studied FAZs. CH\(_2\) scissor vibrations are appeared in the region 1300-1500 cm\(^{-1}\). Two separate peaks although with low intensity are noticeable at Samples 2, 4 and 5, and are barely hinted at the other two patterns. IR spectra are indicative of the beginning of a catalytic process of conversion of CO\(_2\) to hydrocarbons, but for a more definite result it is necessary to conduct further studies at higher pressures.

![FT-IR spectrum of samples exposed to CO\(_2\) for Case 2 and regions of bands vibration for O-H, C-H, and C-O.](image1.png)

**Figure 1.** FT-IR spectrum of samples exposed to CO\(_2\) for Case 2 and regions of bands vibration for O-H, C-H, and C-O.

Regarding to the reaction’s mechanism it is supposed that the hydrogen radicals for the catalytic hydrogenation of CO\(_2\) are provided by acidic Brønsted centers in FAZ structure, while the catalytic performance of Fe\(^{2+}/\)Fe\(^{3+}\) active centres is ascribed to the reduction of iron oxides forming the intermediate iron carbides. The mechanism of CO\(_2\) catalytic conversion to hydrocarbons onto FAZ is shown on figure 2.

![Mechanism of CO\(_2\) catalytic conversion to hydrocarbons onto FAZ.](image2.png)

**Figure 2.** Mechanism of CO\(_2\) catalytic conversion to hydrocarbons onto FAZ.

4. **Conclusion**
The experimental investigation of CO₂ conversion of hydrocarbons at low pressure were performed at equilibrium condition for 18 hours and 114 hours. At the short time of exposure, the physical adsorption is established for the all studied FAZ confirmed by gravimetric and FT-IR analyses. The beginning of catalytic reaction is observed for the sample with S_{BET}=404 m^2/g and highest content of hematite due to the high temperature treatment during the synthesis procedure. The longer time of CO₂ exposure leads to the appearance of C-H band vibration on FT-IR spectra and a slight change in the weight of the system is also observed due to the catalytic reaction. It is established that the well-developed surface of materials intensifies the reaction of CO₂ conversion to hydrocarbons. For the clarification of mechanism and quantification of obtained results additional studies will be performed. The proposed mechanism of hydro-carbonization is similar to those at the Sabatier reaction for which is required high energy supply (\Delta H = -164.9 kJ/mol) and free hydrogen. The combined system for carbon capture and unitization in the production process of synthetic gas is low energy approach for CCU installation situated at the power plant site. The further optimisation of FAZ application as triple system for adsorbent-carrier-catalyst will be directed to experimentally investigation of the effect of pressure and time on the CO₂ catalytic conversion processes.

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