

# Coal ash zeolite as a self-catalytic-chemisorption system for conversion of carbon dioxide to hydrocarbons

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## Abstract

In our study, initial attempts on the conversion of carbon dioxide to hydrocarbons based on the catalytic activity and the atmospheric moisture-retaining ability of coal fly ash derived zeolites (FAZ) are provided. The experimental investigations on the CO<sub>2</sub> chemisorptions were performed in a static reactor at pressure of 5.5 MPa over FAZ of Na-X type. The conversion of CO<sub>2</sub> to hydrocarbons was established by IR-spectroscopic and differential thermal studies. This study outlines new research challenges for the development of technological solutions for the effective reduction of greenhouse gases by converting CO<sub>2</sub> into synthetic fuels.

**Keywords:** Fly ash zeolites, Carbon capture and utilization, CO<sub>2</sub> conversion to fuels

## 1. Introduction

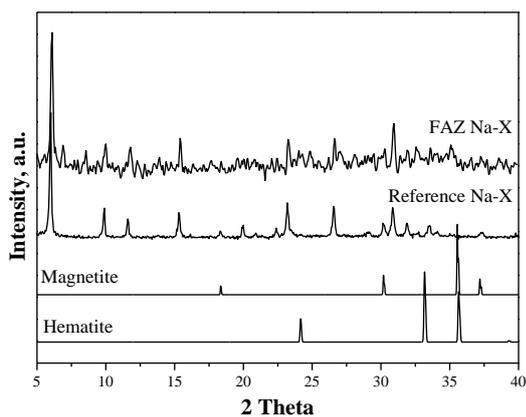
At present, the developments of sustainable carbon capture technologies are of the main scientific and technological priority required to mitigate the over generation of greenhouse gases. Three CO<sub>2</sub> clean energy production approaches have been outlined: pre-combustion capture, oxy-fuel combustion and post-combustion capture. Next challenge for the low-carbon technologies is carbon dioxide recovery instead of its underground storage. A radical discovery for non-fossil fuel energy source is the production of methane from carbon dioxide and hydrogen (Wang and Gong). This process attracts industrial interest after combining it with renewable energy sources to supply electrolysis of water to produce hydrogen and the development of catalysts to accelerate the kinetics of the methanation reaction. However, catalysts are easily deactivated because of sintering and coke deposition (Mebrahtu et al.). In this study, an attempt is presented to capture CO<sub>2</sub> and to convert it into hydrocarbons over coal fly ash zeolites (FAZ). Our hypothesis about the feasibility of FAZ as effective and low-cost catalysts in the methanation of CO<sub>2</sub> is owned to the high concentration of acidic Brønsted centers in their structure providing hydrogen radicals and to the presence of catalytically active iron oxides transferred from the raw coal ash.

## 2. Experimental

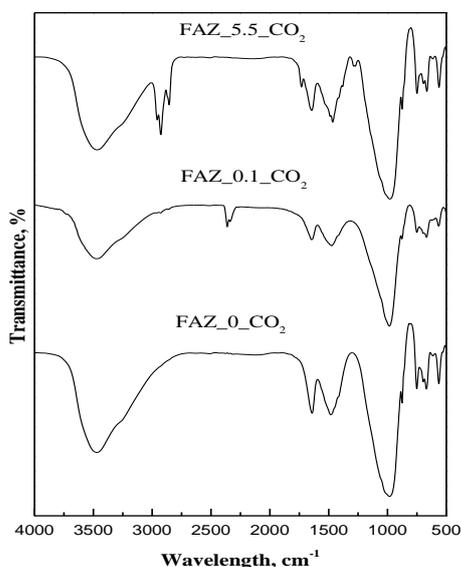
Zeolite Na-X was synthesized by double stage fusion-hydrothermal synthesis from fly ash (FA) of lignite coal collected from the electrostatic precipitators of the biggest TPP in Bulgaria "Maritza East 2". FA and sodium hydroxide as an alkaline activator were mixed in a weight ratio NaOH/FA=2.0 and fused in a nickel crucible at 550 °C for 1 h. The sintered sample was spread in distilled water and continuously stirred magnetically. The reaction slurry was charged in a closed vessel and hydrothermally activated at 90 °C for 2 h. Phase composition of the obtained FAZ was studied by X-ray powder diffraction using Bruker D2 Phaser diffractometer with CuK $\alpha$ -radiation and a Ni filter. Zeolite samples of 1 g were packed in gas permeable bags, placed in a stainless steel reactor and exposed for 2 h into pure CO<sub>2</sub> under pressures of 0.1 MPa (FAZ\_0.1\_CO<sub>2</sub>) and 5.5 MPa (FAZ\_5.5\_CO<sub>2</sub>) ensured by a bruster pump. CO<sub>2</sub> free (FAZ\_0\_CO<sub>2</sub>) and loaded FAZ were studied by Fourier transforming Infrared spectroscopy (FTIR) on a Bruker Tensor 37 apparatus. Differential thermal analyses (TG-DTA) of FAZ before and after CO<sub>2</sub> exposure were performed using analyzer Setsys 2400, Setaram.

## 3. Results and Discussions

X-ray diffractogram of FAZ is plotted in Fig. 1. The main crystalline phase observed is zeolite Na-X, while reflexes of iron oxides transferred from the raw FA can be also found. Preliminary compositional studies reveal around 11 wt.% Fe in the similar specimens (Boycheva et al.). FTIR spectra of FAZ before and after to be exposed to CO<sub>2</sub> are plotted in Fig.2. The peculiarities on the IR spectrum of FAZ\_0\_CO<sub>2</sub> correspond to the typical vibration zones reported for FAZ Na-X (Boycheva et al.).

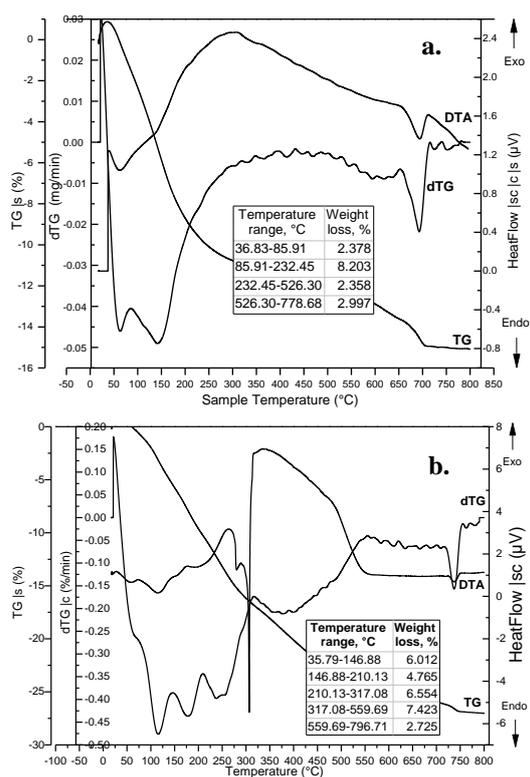


**Figure 1.** X-ray diffractograms of FAZ Na-X and references.



**Figure 2.** FTIR spectra of FAZ and CO<sub>2</sub> loaded FAZ.

At FAZ<sub>0.1</sub>CO<sub>2</sub> an adsorption band is observed between 2390-2290 cm<sup>-1</sup> denoted to the physisorbed CO<sub>2</sub> molecules. A strong adsorption band between 3000 and 2800 cm<sup>-1</sup> is appeared at FAZ<sub>5.5</sub>CO<sub>2</sub> assigned to CO<sub>2</sub> chemical adsorption assuming formation of hydrocarbons. Typical for hydrocarbons are the IR absorption peaks between 3300 and 2800 cm<sup>-1</sup> due to C-H stretching vibrations. It could be also expected that CO<sub>2</sub> chemisorption results in saturated hydrocarbons, because the sp<sup>3</sup> hybridized C-H bonds vibrate between 3000-2800 cm<sup>-1</sup>, while the sp<sup>2</sup> and sp-hybridized carbon bonds are shifted to larger wavenumbers. Accompanying weak chemisorption owing to formation of carbonate and bicarbonate species could be also assumed due to the appearance of small adsorption features at 1730 cm<sup>-1</sup> and 1280 cm<sup>-1</sup>. Comparative TG-DTA studies of FAZ<sub>0</sub> and FAZ<sub>5.5</sub>CO<sub>2</sub> (Figure 3) reveal loss of mass between 210 and 317 °C at the CO<sub>2</sub> loaded sample most likely owing to the thermal realisation of hydrocarbons.



**Figure 3.** TG-DTA curves of FAZ (a) and CO<sub>2</sub> loaded FAZ (b).

#### 4. Conclusions

The obtained results reveal that the pressure swing adsorption of CO<sub>2</sub> onto fly ash zeolites takes place as a chemisorptions process obeyed by catalytic transformation of CO<sub>2</sub> to hydrocarbons. This observation reveals new perspectives for developing of carbon capture and utilization technologies.

#### Acknowledgements

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#### References

- Boycheva S., Zgureva D., Barbov B., Kalvachev Y. (2014), Synthetic micro- and nanocrystalline zeolites for environmental protection systems, In: *Nanoscience Advanced in CBRN Agents Detection, Information and Energy*, Springer, SSPS Series-A: Chemistry and Biology, Eds. Petkov P. et al., pp. 443-450.
- Mebrahtu C., Krebs F., Abate S., Perathoner S., Centi G., Palkovits R. (2019) Chapter 5 - CO<sub>2</sub> methanation: principles and challenges, In: *Studies in Surface Science and Catalysis* Eds.: Albonetti S. et al., Elsevier, **178**, 85-103.
- Wang W., Gong J. (2011), Methanation of carbon dioxide: an overview, *Front. Chem. Sci. Eng.*, **5**, 2-10.