Comparative studies of the equilibrium adsorption of CO_2 onto coal ash zeolites Na-X and Na-Ca-X

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Abstract

Coal-fired Thermal Power Plants (TPPs) are the main source of greenhouse gas emissions in the atmosphere, but they also generate huge amounts of solid by-products, including fly ash (FA). Thanks to its aluminosilicate nature, FA is investigated to be converted into zeolites for applications in gas cleaning systems. The development of technologies for CO_2 capture by fly ash zeolites (FAZ) will provide a join solution for the two main ecological problems concerning coal supplied TPPs, namely utilization of solid residues and implementation of carbon capture technologies. In the present study, the comparative studies were performed on the adsorption of CO_2 onto FAZ of Na-X and Na-Ca-X types in relation to their specific surface and porosity.

Keywords: fly ash zeolites; carbon capture technologies; solid sorbents, CO_2 adsorption

1. Introduction

Coal combustion thermal power plants (TPPs) are the major producer of energy. However, coal supplied TPPs generates numerous by-products, which can cause local and transboundary pollution. These pollutants are solids, e.g, coal fly ash (FA), and gases, such as sulfur oxides, nitrogen oxides, and carbon oxides. Carbon dioxide (CO_2) is the main greenhouse gas with the highest contribution to the global warming, therefore variety methodologies to reduce carbon emissions are under development (MacDowell et al.). The purpose of our research is to investigate zeolites synthesized from fly ash (FA) with high porosity and good surface characteristics in terms of their equilibrium CO_2 adsorption capacity (Zgureva). The development of technology for CO_2 capture by coal fly ash zeolites (FAZ) will contribute for finding decisions of two main ecological problems of significant importance for coal supplied TPPs – utilization of solid residues and implementation of low-carbon process. Zeolites are a large group of aluminosilicate natural or synthetic minerals which are characterized with unique porous structure obeyed by three dimensional framework composed of silica and alumina tetrahedra bonded by oxygen bridges that determines their good potential for adsorption and desorption. The negative charge at alumina tetrahedra is compensated by metal cations, which will most probably influence the adsorption properties of zeolites. Here, comparative studies of CO_2 adsorption potential of FA-derived zeolites of Na-X and Na-Ca-X types were performed.

2. Experimental

FAZ were obtained from FA collected from the electrostatic precipitators of two different TPPs in Bulgaria TPP “AES Galabovo” (FA_{AES}) and TPP “Maritza 3” (FA_{M3}). Both raw materials are referred to class F according to the standard specification of coal fly ash (ASTM 618) but the contents of CaO differs significantly 3.01 wt % for FA_{AES} and 9.36 wt. % for FA_{M3}. Zeolitization of both FAs was performed by double-stage fusion-hydrothermal alkaline activation. FA and NaOH mixtures in a ratio 1:2 are fused at 550 °C, diluted in distilled water and sonicated for 15 min. The subsequent hydrothermal treatment of the reaction slurries was carried out for 4h under 90°C. The precipitates are filtered, washed repeatedly with water, and dried at 105°C for 1 h. Surface studies of FAZ were performed via N_2-adsorption/desorption isotherms measured in an apparatus TriStar II 3020, Micromeritics at 77 K. FAZ were preliminary degassed in a set-up FlowPrep 60 at 260 °C for 4h under He flow. The adsorption/ desorption experiments were performed at 92 points in the range of p/p_0 = 0.0002-0.996, where $p_0 \approx$ 94.9 kPa is the N_2 saturated pressure at 77 K. Specific surface areas (S_{BET}, m^2/g) were evaluated applying the multi-point Brunauer–Emmett–Teller (BET) model, while micro- and mesoporosity were studied by t-plot and Barrett-Joyner-Helenda (BJH) models. Adsorption tests were performed at precisely regulated pressures of pure CO_2 gas carried out through laboratory tubes loaded with synthesized FAZ. Adsorption isotherms were built performing measurements in sets of 25 points in equilibrium conditions as a function of the CO_2 adsorbed quantity and the gas relative pressure p/p_0, where $p_0 \approx 3485.6769$ kPa is the CO_2 saturated pressure at 0 °C. The experiments were performed in a water-ice bath in the relative pressure range p/p_0 = 0.001–0.03. Langmuir computational model was applied to describe CO_2 adsorption isotherms.

3. Results and Discussions

FAZ obtained by FA_{AES} and FA_{M3} are dominated by zeolite X type, as revealed by their preliminary X-ray diffraction studies and are denoted as Na-X and Na-Ca-X, correspondingly. The results from their surface studies are summarized in Table 1 and N_2 adsorption/desorption isotherms are plotted in Fig. 1.

Table 1. Surface characteristics of FAZ

Surface parameters	**Na-X**	**Na-Ca-X**
S_{BET}, m^2/g	432	421
V_{total}, cm^3/g	0.30	0.30
V_{micro}, cm^3/g	0.11	0.12
V_{meso}, cm^3/g	0.19	0.18
d_{micro}, Å	14	14
d_{meso}, Å	44	53

S_{BET}-specific surface; V_{micro}, V_{meso}, V_{total} – internal volume described by micro and mesopores, and total pore volume, correspondingly; d_{micro}, d_{meso}- average micro and mesopore sizes.

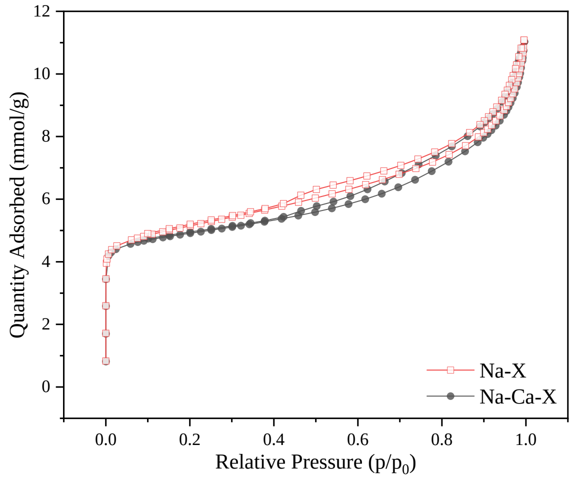

Figure 1. Surface isotherms of Na-X and Na-Ca-X

Both FAZ exhibit isotherms close to type IV (IUPAC, 1985), which are typical for solids with mixed micro- and mesopore structures. Zeolites Na-X and Na-Ca-X are characterized with similar surface parameters, however, the first specimen has little superiority to the specific surface, whereas the high calcium zeolite has mesopores with larger diameters. The experimental and model CO_2 adsorption isotherms are plotted in Figure 2. The adsorption increases along with the pressure as at low p/p_0 the micropore filling occurs followed by continuous adsorption in mesopores at higher p/p_0. The progressively increasing trend of the adsorption with pressure increase is better pronounced at the isotherm of FAZ Na-Ca-X. In the studied pressure range, FAZ saturation with CO_2 was not achieved for both samples.

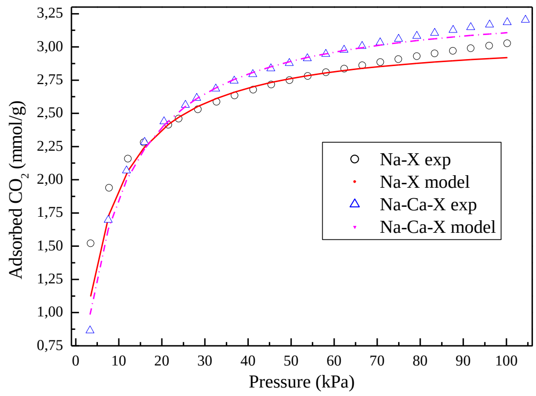

Figure 2. Experimental and model CO_2 adsorption isotherms of FAZ Na-X and Na-Ca-X.

It was found that the experimental adsorption isotherms for both FAZ are in good agreement with the Langmuir mode R^2>0.99, described as follows:

$$\frac{V}{V_0} = \frac{bP}{bP+1} \qquad (1)$$

Where V_0, mmol/g and b, kPa^{-1} are adjustable parameters. The estimated parameters of the Langmuir model are listed in Table 2. The equilibrium adsorption capacity C_{ads} of FAZ at 100 kPa, which is the common pressure of the flue gases emitted by the stacks, is reported in Table 2.

Table 2. Langmuir model parameters and CO_2 adsorption capacity of FAZ

Sample	**V_0, mmol/g**	**b, kPa^{-1}**	**C_{ads}, mmol/g**	**C_{ads}, mg/g**
Na-X	3.10	0.1653	3.026	133.14
Na-Ca-X	3.36	0.1244	3.185	140.14

4. Conclusions

Fly ash zeolites with higher calcium content reveal better adsorption ability toward CO_2 as compared to their natrium-enriched analogues. This observation is meaningful for development of efficient adsorbents for carbon capture technologies.

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References

MacDowell N., Florin N., Buchard A., Hallett J.,. Galindo A, Jackson G., Adjiman C., Williams Ch., Shah N., Fennell P. (2010), An overview of CO_2 capture technologies, Energy Environ. Sci., **3**, 1645–1669 |

Zgureva D. (2016), Carbon dioxide adsorption studies on fly ash zeolites, *CCGP*, **8**, 54-59.