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Chemically Modified Wasted Fly Ash from the Konin Power Plant and its Adsorption Properties

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Abstract

On the basis of X-ray diffraction, infrared spectroscopy, and thermogravimetry examinations, it was concluded that chemically modified lignite fly ash showed a zeolite-like structure. It was found that the zeolitized coal ash samples were effective adsorbents for n-butylamine removal.

Keywords: fly ash, zeolite-like structures, n-butylamine adsorption.

Introduction

Fly ash is the main waste product of the power industry generating thermal energy from solid fuel.

From a chemical point of view fly ash is a mixture of oxides of different compositions dependent on the type of coals subjected to combustion. Analysis of the composition of fly ash enables us to conclude that they are aluminosilicates whose properties make them similar to vulcanized ash. Moreover, these ashes contain sodium, potassium, phosphorus, iron, chromium, copper, nickel, zinc, manganese, titanate, molybdenum, arsenic, and other elements [1].

The physicochemical similarity of fly ash to aluminosilicates and aluminosilicate vulcanized ash suggests their susceptibility to transformation into zeolite-like crystalline structure materials under the influence of appropriate chemical treatment [2,3].

The aim of the present paper is to study the synthesis of materials improved via chemical treatment of waste fly ashes from Konin Power Plant and their applicability as adsorbents of chemical pollution of the natural environment.

Experimental

Modification of Fly Ash

20g of fly ash, labelled ZS-13, from the Konin Power Plant was combined with 160 cm^3 3.5 M solution of NaOH and heated under reflux condenser at 90-100°C for 24 hrs, and then filtered off and washed with distilled water until pH=7. The obtained material was dried at 120°C for 12 hrs.

The same procedure was applied to obtain other modifications of ash using solutions of 4g NH_4HCO_3 and 160 cm^3 of NaOH, 200 cm^3 of 2.5 M HCl, and 4g of EDTA in 100 cm^3 of water.

The samples obtained after modification were labelled as follows: ZS-13 NaOH, ZS-13 NH_4HCO_3/NaOH, ZS-13 HCl and ZS-13 EDTA.

Diffractometric Studies

The obtained modifications and the starting fly ash was examined on a TUR M-62 diffractometr using CuKa radiation and Ni filter (l=l.5418 Å)

IR Spectroscopy Studies

The studies were performed on a Perkin-Elmer Model 180 spectrometer within the range 1800-400 cm^{-1}, using 1.5 mg sample mixed with 200 mg of KBr and pressed into a thin tablet.

Thermal Studies

The studies were performed on a OD-102 derivatograph. The ash was heated in a ceramic crucible in the air under

the following conditions: balance sensitivity: 200 mg; heating temperature: 20-1000°C; DTA 1/5 TG sensitivity: 200 mg; heating time: 100 min; heating rate: 10°C/min; reference material - a-Al_2O_3.

n-Butylamine Adsorption

Adsorption on the modified and unmodified samples was studied by the gas chromatography method using n-butylamine as adsorbate. Adsorption studies were carried out in a reactor (100 mm long, 10 mm diameter) with an installed steel mash which was subsequently covered first by 1 cm of quartz wool, then by 0.1 g adsorbent (±0.0002 g), and finally by a 1 cm layer of quartz wool.

The reactor was connected to a W. Giede-18 gas chromatograph through which a nitrogen stream as a carrier gas was passed at the rate of 30 cm^3/min.The adsorbent was activated at 450°C for 2 hrs, and then the temperature was lowered to 100°C and kept constant for 1 h. Then on the adsorbent, 10 ml of n-butylamine was injected through a Zimmermann syringe and determined chromatographically by comparing the peak surface area prior to and after adsorption of n-butylamine. In order to evaluate adsorbent deactivation, under the above conditions 5 subsequent impulses (10 ml) were introduced at 15-minute intervals.

Results and Discussion

Fig. 1 shows diffractograms of the starting fly ash ZS-13 and its chemical modifications. The aim of these studies was to determine crystalline ordering of the obtained products. The starting fly ash reveals a number of well-resolved crystallographic reflexes (Fig. la), among which the most distinguished are two reflexes of a significantly high intensity for interplanar distances d=3.84, 3.30 Å and a few smaller reflexes: with d=2.83, 2.73, and 2.67 Å. Chemical modification with NaOH solution (Fig. 1b) leads to disappearance of a big reflex d=3.48 Å and a few smaller ones: 2.67 Å and 2.39 Å and simultaneously to an increase of reflex with a high intensity d=3.02 Å. For fly ash modified with a mixture of solutions of NH_4HCO_3 and NaOH (Fig. 1c) the same reflexes as above are observed. However, intensity of the reflex with d=3.02 Å is higher, and that of the reflex with d=3.30 Å slightly lower, whereas the position and intensity of the other reflexes are similar. The sample obtained through chemical treatment of fly ash with HCL solution (Fig. ld) reveals two reflexes of high intensity (d=3.33, 4.23 Å) and a shift of a reflex observed in the previous modification from 3.02 Å to 2.98 Å and a significant decrease in its intensity. Moreover, two new reflexes with d=1.81 and 1.37 Å and of a relatively low intensity are observed. Application of EDTA as an agent to modify the structure of fly ash (Fig. 1e) results in considerable shrinkage of reflexes relative to the corresponding ones in the starting material, except for reflex 3.33 Å, whose intensity in both cases is similar. Formation of new crystallographic reflexes and increase in the intensity of some of them are related to development of new crystalline structures or increasing crystalline ordering of the existing structures (Fig. 1 b-c). Ordering of the structures is related to dealumination and removal of some ions of heavy metals found in the examined ash and ionic exchange of cations, e.g. in c and d samples (Fig. 1.).

The IR spectrum of the starting ash ZS-13 (Fig. 2a) shows in the range 1600-400 cm^{-1} a few clear adsorption bands (at 1125, 675, 610, 590, 505 cm^{-1} and a few weak (at 460, 800 cm^{-1}) as well as broadened ones in the range 1000-900 cm^{-1}.

Chemical treatment with the solution of NaOH (Fig. 2b) and NH_4HCO_3/NaOH leads to disappearance of a broad band at 1125 cm^{-1} and bands at 675, 610, 590, and 505 cm^{-1} . Instead, strong bands at about 1420-1410, 975-965 and 440 cm^{-1} appear. In the case of fly ash modification with a solution of hydrochloric acid, a spectrum of the obtained sample (Fig. 2d) reveals well- distinguished bands at 1145, 1085, 790, 650, 595, and 465 cm^{-1}. On the other hand, a spectrum of the sample obtained as a result ot modification with EDTA solution (Fig. 2e) shows broad bands of a relatively high intensity at 1375, 1005 cm^{-1}, and low intensity bands at 835, 750, 510, and 410 cm^{-1}.

On the basis of former studies [1,2,3] it can be concluded that hydrothermal treatment with the applied solutions gives products of a relatively well developed zeolite structure, which is evidenced by absorption bands characterizing vibrations among tetrahedras $Si(Al)O_4$ as elements of the structure of zeolite crystalline lattice.

Heating fly ash and its modifications to the temperature of 1000°C is described by curves indicating thermal effects (DTA) and mass loss (TG). Fig. 3a shows these curves for fly ash ZS-13. It was found that heating the samples brings about a small mass loss which attains only 1.5% wt.%. The DTA curve exhibits exothermal effects with maxima at 140, 440, and 880°C. TG and DTA curves exclude a presence of zeolite structures.

On the other hand, chemical modifications with NaOH (Fig. 3b) and NH_4HCO_3/NaOH (Fig. 3c) give similar TG and EDTA curves. On the TG curve one may distinguish three sections corresponding to three-stage mass loss: 20-450, 450-750, 750-820°C. The sections are related to some energetic effects. So, for the first section one may see weak endothermal effects and a large exothermal effect with a maximum at 400 and 500°C for the modification with NaOH (Fig. 3b) and 340°C for modification with NH_4HCO_3/NaOH (Fig. 3c). The second stage of mass loss is not related to any specific thermal effect, while the third is accompanied by a distinct endothermal effect with a minimum at 800-820°C, which is directly connected to the exothermal

effect with the maximum at 850°C. The latter is not related to mass loss. In the case of the other two modifications (Fig. 3 d, e) another type of effect is observed. Mass loss is significantly lower than in the two above-mentioned cases and it is equal to 11 and 15%, respectively.

Ash modification with HCl exhibits a small effect with a minimum at 140°C accompanied by mass loss and a large exothermal effect with a maximum at 410°C accompanied by a relatively small mass loss. The DTA curve of a sample obtained through treatment with

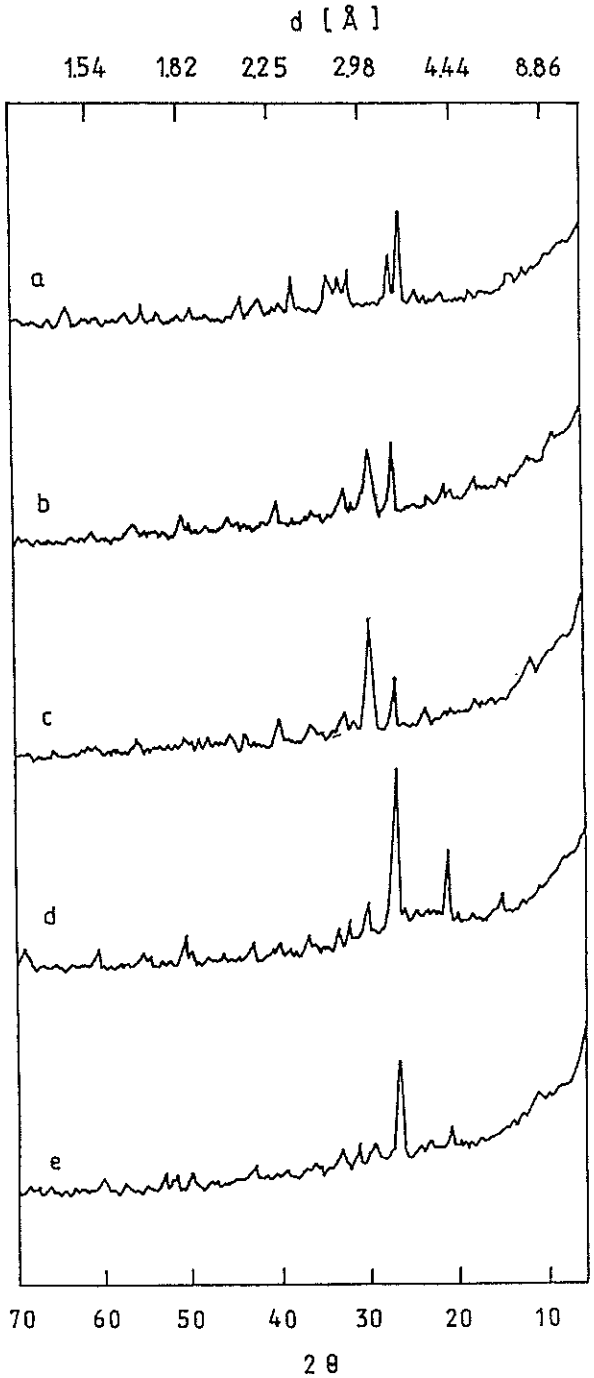


Fig.1. X-ray powder diffraction paterns of fly ash and its chemical modification.

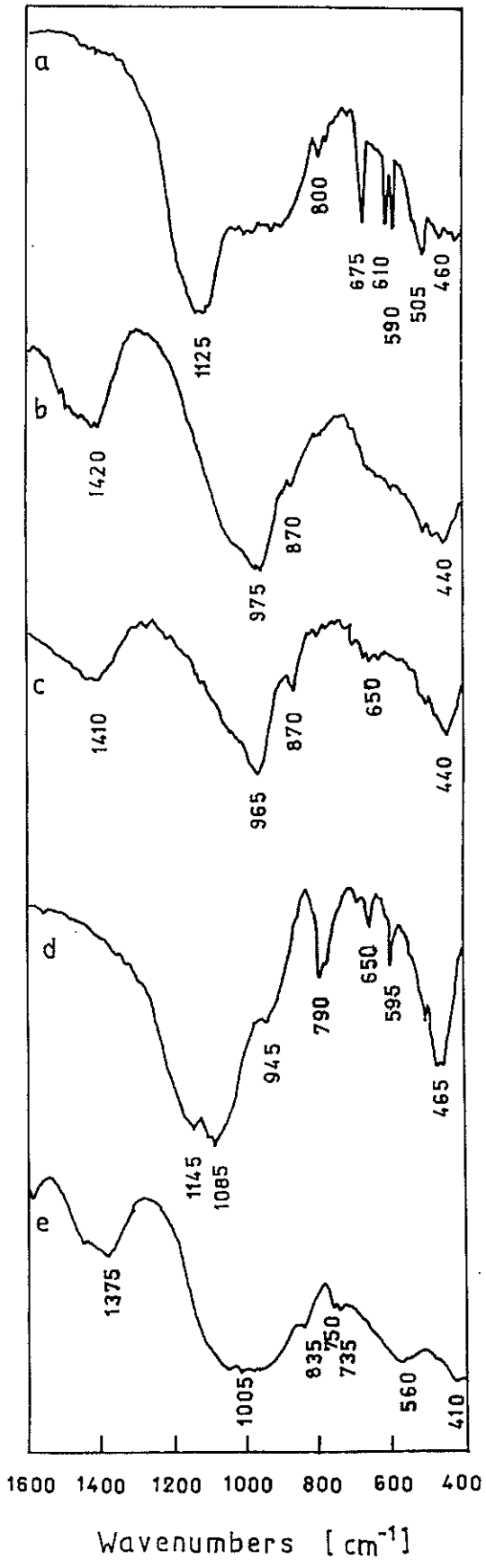


Fig.2. Infrared spectra of fly ash and its chemical modifications

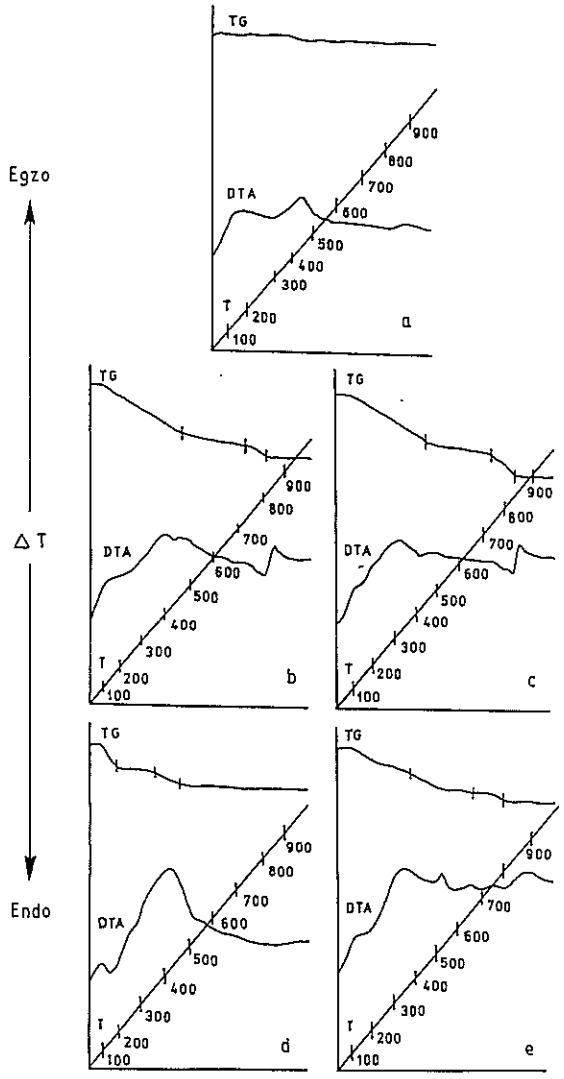


Fig.3. Differential thermal curves of fly ash and its chemical modifications

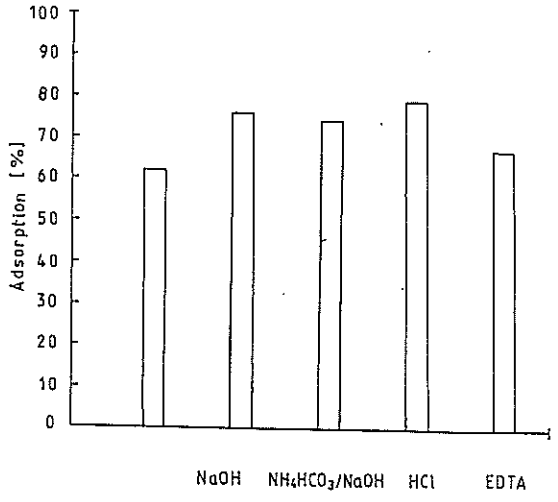


Fig.4. n-Butylamine adsorption on fly ash and its chemical modification

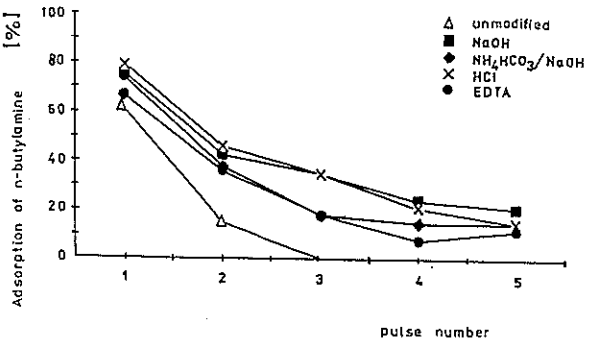


Fig.5. Adsorption stability of fly ash and its modification

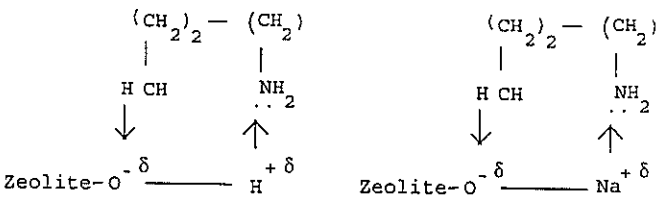
EDTA reveals the presence of two small endothermal effects: the first is seen as a weak shoulder at 190°C, and the second with a minimum at 780°C. In addition, there are some very distinct exothermal effects with maxima at 350, 510, 640, 720, and 850°C. Effects occurring below 750°C are accompanied by mass loss, yet further heating does not lead to a detectable loss.

The adsorption properties of the modified fly ash was tested in the process of amine removal from a gas-phase. Compounds of this type are produced during product decay e.g. in food and fish processing plants made of protein, and may also be found in the textile (synthetic fibre) and pharmaceutic industries and in the production of surfactants. Butylamine is a typical model compound applied in studies on deoderization of atmospheric air.

As follows from the results presented in Fig. 4, the obtained samples and the starting ash may be ordered according to an increasing adsorption capacity in the following sequence:

$$ZS-13 < \frac{ZS-13}{EDTA} < ZS-13-\frac{NH_4HCO_3}{NaOH} < ZS-13NaOH < ZS-13HCl$$

The highest adsorption ability was observed for a sample obtained by fly ash modification with hydrochloric acid. It was already shown in the past that treatment of kaolin, bentonite with acid or of another clay with acid leads to highly acidic zeolite structures [5,6]. It can be supposed therefore that adsorption of n-butylamine proceeds mainly on a zeolite acid surface, which is shown in Scheme a.



a b

On the other hand, in the case of a less active sample obtained by modification with a solution of sodium hydroxide it was found that such a modification increases the crystalline ordering of the element's structure or even causes a phase transformation [7,8]. In this case, n-butylamine molecule reacts with surface zeolite species according to Scheme b.

Adsorption stability of the studied samples was defined by the number of subsequent pulses of n-butylamine (1 pulse-l0μl) introduced on adsorbents at 15-minute intervals (Fig. 5). It follows from the conducted studies that with an increasing number of pulses the adsorption ability decreases. The presented results show that adsorption activity of the unmodified fly ash ZS-13 disappear quite rapidly, while the adsorption ability of its chemical modifications remains considerably high.

Results afforded by the present paper indicate that by chemical modification of wasted fly ash from the Konin Power Plant it was possible to obtain adsorbents of a zeolite-like structure and of a relatively high n-butylamine adsorption.

Taking into account similar pk_a values of homologic row of aliphatic amines we can suggest in these cases the same adsorption mechanism.

However, for other polar aliphatic compounds such as alcohols and mercaptans, interaction between their functional groups and adsorption centres will be weaker. For these compounds adsorbents with stronger acid functions should be recommended.

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