III. MAN AND BIOSPHERE

CONVERSION OF COAL FLY ASH TO ZEOLITE-BASED IRON OXIDE MAGNETIC NANOCOPOSITES BY MODIFIED FUSION-HYDROTHERMAL SYNTHESIS

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Abstract. Coal fly ash generated in Thermal Power Plants is utilized for synthesis of zeolites due to its aluminosilicate composition. The highest degree of zeolitization of coal ash in a particular zeolite phase is achieved by double-stage synthesis involving successive alkaline melting and hydrothermal activation of the reaction mixtures, while the uniform distribution of the iron oxides transferred from the raw coal ash is ensured by ultrasonic treatment. However, the applied melting step results in the oxidation of the magnetic iron oxide phases to non-magnetic ones, which results in the loss of magnetic properties of the resulting materials. The present investigation focuses on an improved double-stage synthesis procedure by the addition of raw coal ash containing magnetite between high temperature and low temperature processing. In this way, the magnetic phase is retained in the final product and the magnetic properties of the zeolites are preserved, which is important for their application in the adsorption of pollutants from wastewater.

Keywords: coal ash utilization, coal ash zeolites, magnetic adsorbents, water treatment, nanoactivated zeolites.

INTRODUCTION

Zeolites are porous natural or synthetic crystalline aluminosilicates with ion-exchange properties that are widely used in water treatment technologies [1]. Due to their broad specific surface values these materials are efficient adsorbents of organic pollutants, heavy metals, ammonia, phosphates etc. from contaminated water effluents [2-4]. Another important advantage of zeolites is their harmlessness to the environment and human health. As the zeolites have a wide industrial use such as adsorbents, dryers, catalytic carriers, molecular sieves, ion exchangers, infiltration barriers, and many advanced applications, the consumption of these materials is increasing progressively [5]. In this regard, the possibilities for synthesizing them from waste aluminosilicates have been intensively explored [6]. The utilization of variety of solid wastes containing silica and alumina by their conversion to zeolites, in addition to meeting the industrial demands of these materials, also leads to a number of environmental benefits, such as the reduction of landfilled wastes and the saving of natural resources. A huge source of waste aluminosilicates is the ash from coal combustion in Thermal Power Plants in generation of electricity. The utilization of coal fly ash by its conversion to zeolites has been widely studied since it is a source of more than 70 wt. % of SiO_2 and Al_2O_3 [7]. The synthesis of zeolites from coal ash is based on the alkaline dissolution of the aluminosilicates contained in it, creating the conditions for the formation of hydrogel and its heterogeneous crystallization in zeolite phases. The production of zeolites from coal fly ash (CFAZ) is a feasible process for

industrialization and can be reliably managed to achieve a high conversion rate in a particular zeolite phase. CFAZ have also been widely studied as adsorbents for wastewater recovery and they have shown high efficiency in the retention of heavy metals and dyes [8, 9]. The adsorption is a basic technique for the purification of waste waters from metal ions, organic compounds, radionuclides, etc. In combination with magnetic separation of the adsorbent particles, it becomes a modern and environmentally friendly water treatment technology, as it reduces wastewaters and eliminates the addition of flocculants [10]. One of the advantages of CFAZ in comparison to their analogues derived from pure substances is that CFAZ contain iron oxides, which are transferred in their structure from the raw coal ash. Applying appropriate homogenization techniques to the reaction mixtures during the zeolite synthesis, the iron oxides can be finely and uniformly distributed in the structural frameworks as nanosized particles [11]. The presence of iron oxides increases the adsorption potential of zeolites to heavy metals due to the increased instauration of the surface and the formation of intermetallic aggregates. In addition, spinel iron oxide phases impart magnetic properties to zeolites. For these reasons, the activation of zeolites with magnetic nanoparticles has been extensively investigated in the development of new adsorbents [12]. CFAZ are the most often prepared by two synthesis procedures, namely hydrothermal and double stage fusion-hydrothermal activation [13]. Hydrothermal synthesis is carried out at mild temperatures; however, a major disadvantage of this method of coal ash zeolitization is that the obtained products are mixtures of zeolitic

phases in relatively small yields. This ash conversion procedure has a major advantage that due to the low thermal treatment the transfer of all iron oxide phases from the starting material to the zeolite is ensured. Double stage fusion-hydrothermal alkaline activation of coal ash results in a particular zeolite phase with considerable yield. At this synthesis procedure a fusion step between 500 and 800 °C is performed prior to the hydrothermal treatment. In this case, however, the zeolites obtained do not have magnetic properties, since the magnetic iron oxides are oxidized thermally

to non-magnetic during the high-temperature processing [14]. To impart magnetic properties, the CFAZ obtained by two-step synthesis are activated by magnetite nanoparticles by adding pre-formed Fe_3O_4 particles to the reaction mixture between the high temperature and low temperature processing, making expensive otherwise low-cost adsorbents [12].

The present study aims to elucidate the possibility of producing magnetic zeolites from coal fly ash while retaining the advantages of two-step synthesis and using magnetite from the raw material.

EXPERIMENTAL

The synthesis procedure is presented in the following scheme:

Fig. 1. Consequence of the laboratory experiments.

The raw coal fly ash and thus prepared CFAZ samples were characterized with respect to their morphology and chemical composition using ZEISS SEM EVO 25 LS-EDAX Tident spectrometer at acceleration voltage of 20-15 kV and electron beam current of 500-150 pA. The phase studies were performed by X-ray diffraction (XRD) technique on a Brucker D2 Phaser diffractometer with CuK α -radiation and a Ni filter.

RESULTS AND DISCUSSIONS

The raw fly ash used as a raw material for these studies is generated from the combustion of lignite coal from “Maritza east” basin in Thermal Power Plant “AES Galabovo”.

SEM images of CFA and the obtained samples upon its zeolitization are presented in Fig. 2. Obviously,

CFA is composed of agglomerates with $d_{50} < 0.045$ mm (Fig. 2a). The agglomeration is due to the high cooling rate of the CFA particles as they pass from the combustion chamber to the dust collector. CFAZ obtained by modified double-stage synthesis consist of crystallites of submicron sizes due to the ultrasonic disproportion of the parent and the alkaline fused raw material into the reaction slurry (Fig. 2b, c). Ultrasonication provides excellent dissolution of the raw aluminosilicates into the alkaline media and fine fragmentation of the insoluble particles that further serve as seeds for heterogeneous crystallization of the aluminosilicate hydrogel. However, it was observed finer morphology at CFAZ obtained by the traditional double-stage synthesis without interim addition of CFA (Fig. 2d). This is because of the better fragmentation of the alkaline fused raw material upon

the ultrasonic treatment as compared to the non-fused CFA. SEM images of CFAZ obtained by modified synthesis reveal the presence of two shapes of crystallites that most probably belong to two zeolite phases (Fig. 2 b, c). It could be expected that the spherical particles belong to zeolite of sodalite type (Fig. 2c), while the hexagonal crystallites are of

cancrinite zeolitic phase (Fig. 2b). Because the sodalite and cancrinite zeolites have the common chemical formula of $\text{Na}_6(\text{Al}_6\text{Si}_6\text{O}_{24}) \cdot 2\text{NaY} \cdot 6\text{H}_2\text{O}$, they are usually formed simultaneously [15]. At similar conditions by traditional double-stage synthesis well-formed hexaoctahedral crystals belonging to a zeolite of the Na-X type, are commonly observed (Fig. 2d).

Fig. 2. SEM images of CFA (a) and CFAZ with (b, c) and without interim adding of CFA (d).

The chemical compositions from the EDX analysis of the raw material and the CFAZ obtained by modified synthesis are presented in Table 1.

Table 1. Chemical composition of CFA and CFAZ

Component	SiO ₂	Al ₂ O ₃	Na ₂ O	MgO	CaO	FeO	K ₂ O	TiO ₂	SO ₃
	Content wt %								
CFA	62.14	26.63	0.57	1.40	1.97	3.87	1.18	1.73	0.49
CFAZ	44.69	25.95	15.11	1.04	4.54	7.24	-	-	1.43

Into the CFAZ composition significant amounts of SiO₂ and Al₂O₃ are established (about 70 wt. %, totally), which is indicative for high extent of zeolitization. In confirmation of this, no unreacted fly ash was observed on the SEM micrographs. The percentage of Na₂O is significantly exceeded into the synthesis product due to the incorporation of

Na⁺-ions from the alkaline activators used as compensating cation in the structural framework of the obtained zeolite. Some components such as K₂O and TiO₂ are not transferred from CFA to CFAZ. However, the weight percentage of iron oxides is substantially increased in the reaction zeolitic product. This result is mostly due to the coal ash

additives at the modified synthesis. X-ray diffractograms of the raw CFA and the obtained CFAZ are plotted in Fig. 3. For the identification of the crystalline phases, comparisons are made of experimental and reference diffractograms of expected zeolites (SOD - sodalite, CAN - cancrinite, NAT - natrolite, LTA - linde A), iron oxides (HEM - hematite, α -Fe₂O₃; MAG-Magnetite, γ -Fe₃O₄). The main diffraction reflex of the quartz which is the most resistant to alkaline treatment phase which is

usually present in considerable amounts in the raw material is barely noticeable on the X-ray pattern of the product. This indicates that although one-third of the CFA does not pass the melting step, the alkali-resistant phases are dissolved in the reaction mixture and digested in the zeolite crystallization due to the ultrasonic treatment. From the expected zeolite phases, the main reflexes of cancrinite and sodalite are identified on the CFAZ experimental diffractogram.

Fig. 3. X-ray diffractograms of the raw CFA, zeolite product and referent crystalline phases

On the X-ray pattern of the CFA reflexes of magnetite and hematite are appeared, while at CFAZ the main peak of magnetite is only indicated. The state and distribution of the iron oxide phases in zeolites obtained from coal fly ash by ultrasonic-assisted traditional double-stage synthesis has been studied previously [11]. It has been found that significant amount of iron from the hematite obtained upon the fusion stage is converted into its ionic forms. Thus, the absence of a major hematite peak from the diffractogram of the CFAZ can be explained by the fragmentation of hematite to fine nanoparticles which diffract as an amorphous constituent or part of it is incorporated into the zeolite matrix as ions. It has also been found that the iron oxide phases are disproportionate to nanosized particles, ca. 10 nm. Therefore, we can assume fine and uniform distribution of magnetite nanoparticles into the structural framework of the zeolite product composed of hydroxy-sodalite/cancrinite zeolite nanocomposites.

This type of zeolite material is characterized by lower surface values as compared to zeolite Na-X, however, it has revealed significant uptake efficiency for removal of heavy metals from waters [16]. The high removal efficiency of this zeolite composite system can be attributed to ion-exchange mechanism rather than the adsorption. In confirmation of this, the compositional studies reveal higher content of the sodium compensating cation in the hydroxy-sodalite/cancrinite zeolite mixture than in the zeolite Na-X obtained by traditional double-stage synthesis. The modified double-stage synthesis ensures the processing of hydroxy-sodalite/cancrinite nanocomposites at soft conditions giving them magnetic properties for easy separation from the purified water. It is expected that this zeolite nanocomposites will exhibit higher removal efficiency toward heavy metal pollutants because of the larger specific external surface as compared to microcrystalline zeolites.

CONCLUSIONS

The alkaline treatment of the coal fly ash via modified double stage fusion-hydrothermal activation leads to synthesis of hydroxy-sodalite/cancrinite zeolite nanocomposites. Thus obtained coal fly ash zeolites contain finely dispersed magnetite nanoparticles transferred from the interim addition of the raw material between the high thermal and the low thermal synthesis stages. It is expected that the obtained materials will be low-cost efficient magnetic ion-exchangers and adsorbents of heavy metals for remediation of polluted waters.

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