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Microspheres of Fly Ash as a Source for Catalytic Supports, Adsorbents and Catalysts

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Abstract

The present paper reviews the processes of separation of microspheres from fly ash and their possible applications for the creation of catalytic supports, adsorbents and catalysts. To isolate magnetic microspheres and cenospheres of stabilized composition, the process flowsheets of concentrate separation, based on the combination of hydro- or aerodynamic and granulometric classification, followed by the separation in magnetic field of different intensity, were developed. Novel materials based on cenospheres of stabilized composition, such as mesoporous microspherical glasses (specific surface area S_{sp} = 3–50 m^2/g), the supported iron oxide systems (S_{sp} = 50–200 m^2/g), and zeolites are described. Spherical zeolites demonstrated good ion exchange properties of in cesium and strontium removal from the technological solutions. The catalytic properties of Fe_2O_3/cenosphere catalysts and magnetic microspheres in deep oxidation of methane are discussed.

INTRODUCTION

Vast amounts of fly ash produced by power stations require development of the efficient ash utilization processes. The spherical particles called microspheres constitute the substantial part of fly ashes, which are used at the moment mostly in construction and material production industries. But it is known that microspheres reveal outstanding thermal, magnetic and some other properties, combined with the unique spherical design and chemical inertness. These features make them a very promising material for the development on their basis new special products of high technological importance. The present paper reviews the processes of separation of microspheres from fly ash and their possible applications for the creation of catalytic supports, adsorbents and catalysts.

CLASSIFICATION AND RECOVERY OF GLASS CRYSTALLINE MICROSPHERES FROM FLY ASH

The accepted classification of microspheres includes three main groups of different morphology (Fig. 1): bulk microspheres (magnetite Fe_3O_4 or alumosilicate glass spherical particles: (a) crystalline, monolith or (b) porous, (c) cenospheres (hollow microspheres based on alumosilicate glass, in which the ratio of the particle diameter to the wall thickness can reach more than 50) and (d) plerospheres (hollow glass crystalline microspheres filled with tiny spherical particles) [1–3]. In real fly ashes, the ratio between these types of microspheres, as well as their chemical and mineral-phase composition, vary in a very wide range and depend on the nature and composition of initial coal and on the coal combustion modes. From the viewpoint of practical application of microspheres

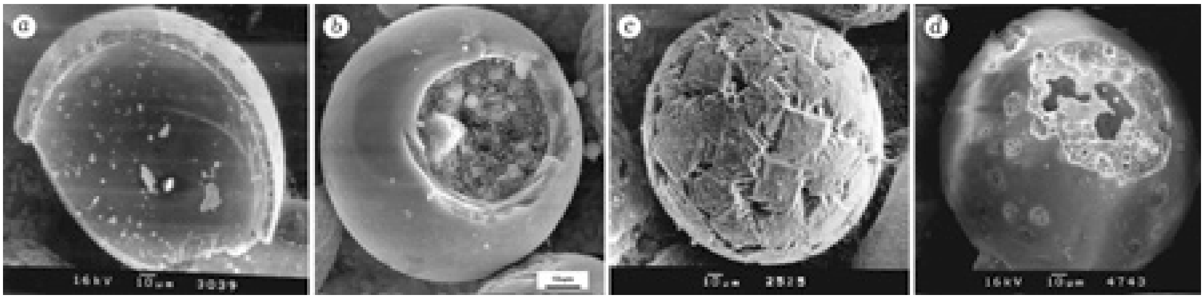

Fig. 1. Typical appearance of the microspheres found in fly ashes: *a* – crystalline microsphere, *b* – porous microsphere, *c* – cenosphere, *d* – plerosphere.

as catalysts and supports, magnetite microspheres with high content of the ferrospinel phase (magnetic microspheres) and cenospheres are the most interesting objects.

The primary separation of fly ash to recover the above-mentioned microspheres includes hydrostatic isolation of cenospheres (concentrate), having the lowest density compared to other ash components (0.3–0.6 g/cm^3), and magnetic separation of the remaining part, resulting in the recovery of magnetic product (concentrate). Concentrates of the microspheres (cenospheres and magnetic microspheres) are mixed materials, that are heterogeneous by their grain size, chemical and mineral-phase composition.

To obtain materials with predictable properties from the microspheres, an additional stabilization of composition of the primary products is required. The further separation of concentrates is based on the difference of physical characteristics of microspheres (density, content of the magnetic constituent, particle size). The process flowsheets of concentrate separation, based on the combination of hydro- or aerodynamic and granulometric classification, followed by the separation in magnetic field of different intensity, have been realized to isolate magnetic microspheres and cenospheres of stabilized composition [4–7].

The scheme to illustrate the principle of hydro- and aerodynamic separation of magnetic microspheres and cenospheres using up-flow or down-flow gas or liquid is presented in Fig. 2. The scheme has been applied to separate the concentrates of magnetic microspheres and cenospheres. As a result, a wide range of microspherical products with stabilized physicochemical properties and chemical compositions has been produced. The detailed study of their properties and morphology by scanning electron microscopy (SEM), Mössbauer spectroscopy, X-ray diffraction (XRD) and electron spin resonance has been carried out. Based on the results obtained, the promising fields of application of stabilized products, including the production of catalysts, supports and adsorbents have been defined and some examples are given below.

MODIFICATION OF MICROSPHERES

Preparation of porous microspherical glasses

The porous structure of glasses is known to be usually formed by removing soluble com-

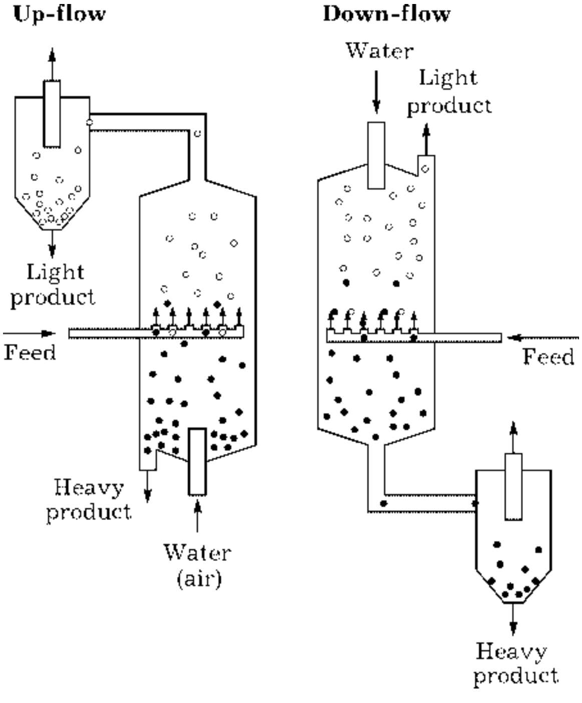

Fig. 2. Scheme of hydro- and aerodynamic separation of concentrates.

ponents from two-phase sodium-boron-silicate glasses as a consequence of chemical etching with mineral acids [8]. Cenospheres can be also precursors of porous glasses due to the presence of acid-soluble phases in the composition of alumosilicate glasses.

The chemical etching of cenospheres was performed by the treatment of non-perforated cenospheres from Novosibirsk power plant with hydrochloric acid at controlled temperature, processing time and volume ratio of sample to etching solution, resulting in the formation of three products, namely two perforated products (P1 and P2) and one non-perforated product (NP) with 4, 20 and 74 % volume yields, respectively (losses – 2 %). All the products have been separated from etching solution, washed with water, calcined at 300 °C and characterized by SEM. Texture parameters of these and other obtained products (specific surface area (S_{sp}), pore volume and pore size distribution) were calculated from the low-temperature isotherms of nitrogen sorption (instrument ASAP 2400 Micromeritics) and from the volume of adsorbed argon at 77 K (method of thermal desorption of argon – TDA).

According to TDA, the S_{sp} of obtained porous cenospheres are equal to 51 m^2/g (P1), 15 m^2/g (P2) and 3.4 m^2/g (NP). For P1, the total single point volume of pores of less than 240 Å at $P/P_o = 0.99$ is as much as 0.016 cm^3/g. For all porous cenospheres, the differential curve of pore size distribution has a well-defined maximum at 35 Å, it spans the range of 50–80 Å pore size, and also shows sufficiently large pores of 100–500 Å. The presence of macropores is also confirmed by SEM. Two types of regular open macropores, having the sizes ≤ 500 Å and 500–5000 Å, respectively, are distinctly observed on the surface of porous cenospheres formed as a result of acid etching.

Thus, the data obtained have shown the possibility to form the mesoporous microspherical glasses with S_{sp} of 3–50 m^2/g based on cenospheres of stabilized composition. Perforation of the cenosphere wall can be reached under these conditions, resulting in the formation of 500–5000 Å open macropores.

Fe_2O_3 supported on cenospheres

The thin films of iron oxide deposited on cenospheres were prepared by the thermal decomposition of iron(III) nitrate on the support surface, including the impregnation of cenospheres with aqueous $Fe(NO_3)_3$ solution of the given concentration and drying at 110–120 °C, followed by calcination of the samples at 500 °C for 2 h and at 600–900 °C for 6 h. Samples with the supported iron oxide content in the range of 0.95–10.1 % mass have been obtained. After every calcination step, the S_{sp} of samples was determined by TDA method using the standard procedure (Table 1). The morphology of iron oxide films was studied by SEM. The S_{sp} of iron oxide was in the range 10–200 m^2/g Fe_2O_3, depending on the Fe_2O_3 content and calcination temperature. The increase of Fe_2O_3 content and calcination temperature results in the decrease of S_{sp}. Thus, the samples with S_{sp} of 50–200 m^2/g Fe_2O_3 and 10–90 m^2/g Fe_2O_3 have been obtained after the calcination at 600 °C and 900 °C, respectively. It is important to note, that according to Table 1 the value of S_{sp} for supported Fe_2O_3 is higher than that for the pure α-Fe_2O_3, treated under the same conditions.

Synthesis and application of zeolite-coated cenospheres

The molar SiO_2/Al_2O_3 ratio for the major fraction of cenospheres is in the range of 2–6, that is very close to the low-silica zeolites. It is known, that low-silica zeolites with FAU,

TABLE 1

Specific surface areas of Fe_2O_3/cenosphere and pure α-Fe_2O_3 catalysts, determined by the thermal desorption of argon

Fe_2O_3 content, % mass	Calcination temperature, °C	S_{sp}, m^2/g Fe_2O_3
2.1	600	200
10.1	600	50
2.1	900	90
10.1	900	10
100 (pure)	600	7.7
100 (pure)	900	3.5

LTA and GIS types of framework are widely used as ion-exchangers, adsorbents and catalysts. Earlier it has been shown by numerous studies, that fly ash can be effectively converted to the up to 13 different zeolitic products by hydrothermal synthesis or alkaline fusion. Process of fly ash conversion to zeolite was evaluated at pilot plant scale [9] and application of such materials for the water treatment technology was suggested [10–12]. The main disadvantage of zeolite produced such way was powder-like character of the resulting materials, which required additional moulding with binder to form granules. Moreover, the substantial heterogeneity of chemical and mineral composition of coal fly ash usually leads to unreproducible results, for example, when the products are being contaminated with iron.

One of the possible ways to achieve a better reproducibility and to eliminate the need for additional granules production is to utilize the glassy microspheres with stabilized composition, obtained by the separation procedures described above.

The zeolitization process was performed in a Teflon vessel at 80–150 °C and autogenous pressure, with 1–4 M aqueous NaOH solution. The XRD, optical and scanning electron microscopy were used to follow the progress of reaction. As a starting material for zeolitization, a fraction of cenospheres with stabilized composition was used, which was additionally purified from magnetic impurities prior to conversion. Depending on the reaction conditions, three types of zeolite frameworks are formed, namely NaA (LTA), NaX (FAU) and NaP1 (GIS), either as a mixture or as a single phase. Formation of zeolite crystals was found to occur both on the surface of cenospheres and in the liquid phase. Longer reaction time results in the total conversion of cenosphere material to zeolites, with the formation of large crystals (3–20 μm), as well as dendrites which are irregularly attached to the surface, the latter process entailing almost complete destruction of cenospheres. When a special attention has been paid to preserve the integrity of cenosphere walls by adjusting process parameters, the tiny crystals of zeolites (<1 μm) were formed, which covered the surface of cenosphere, forming a coating (Fig. 3). Under these experimental conditions, it is possible to fulfil the conversion of the major part of glass phase to zeolites, while keeping intact the initial spherical shape.

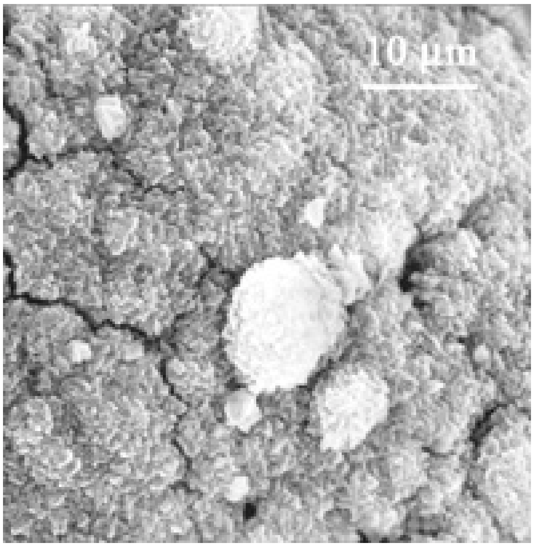

Fig. 3. Zeolite NaA coating on the surface of P1 cenosphere.

These spherical zeolite-containing sorbents were tested as ion-exchangers for cesium and strontium removal from dilute and concentrated technological solutions, and demonstrated up to 2 meq/g total cation exchange capacity and a good selectivity of the heavy metal ion removal.

APPLICATION OF MICROSPHERES IN CATALYSIS

Catalytic properties of Fe_2O_3/cenosphere catalysts in deep oxidation of methane

Catalytic properties of Fe_2O_3/cenosphere catalysts were studied in a microcatalytic setup with quartz fixed bed reactor loaded with 0.1–0.3 g of the catalyst. The calcination temperature dependence of the specific catalytic activity of Fe_2O_3/cenosphere catalysts in the reaction of deep oxidation of methane at 400 °C is presented in Fig. 4. In overall, the experiments have shown that activity depends on the content of Fe_2O_3. Regarding activity dependence on the calcination temperature for each individual catalyst, only those with 1 and 10 % mass of Fe_2O_3 exhibit no dependence (within an experimental error) in the temperature ranges of 600–700 and 500–800 °C, re-

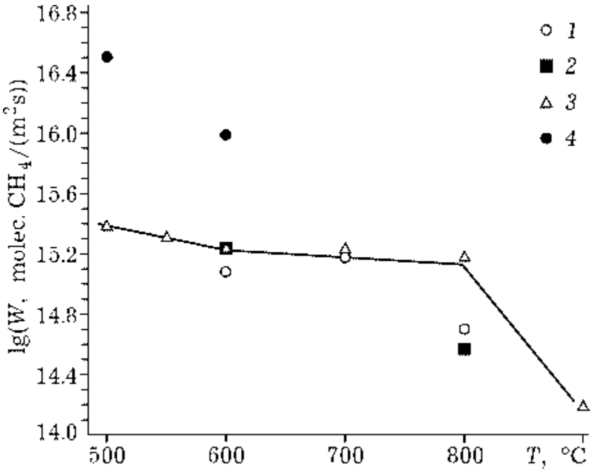

Fig. 4. Variation of specific catalytic activity of Fe_2O_3/cenosphere catalysts in the reaction of deep oxidation of methane as a function of calcination temperature. $CH_4 : O_2 = 2 : 98$; reaction temperature 400 °C; Fe_2O_3 loadings, % mass: 1 (*1*), 2.1 (*2*), 10 (*3*), 100 (*4*).

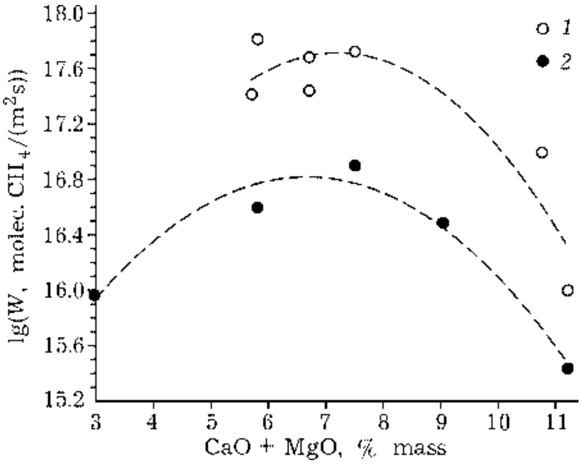

Fig. 5. Variation of specific catalytic activity of magnetic microspheres in the reaction of methane deep oxidation as a function of (CaO + MgO) content: *1* – 520 °C, $CH_4 : O_2 = 85 : 15$ % vol.; *2* – 500 °C, $CH_4 : O_2 = 2 : 98$ % vol.

spectively. The activity of Fe_2O_3/cenosphere catalysts is lower, compared to the pure α-Fe_2O_3. This decrease of activity is likely to be caused by the interaction between iron oxide and catalyst support. It can also be seen, that the activity of pure α-Fe_2O_3 decreases very strongly as a result of calcination temperature rise from 500 to 600 °C.

Catalytic properties of magnetic microspheres in oxidative coupling and deep oxidation of methane

It is known, that catalysts of deep oxidation based on ferrospinels are less active than other oxide systems, in particular, cobaltites and chromites [13–16]. Nevertheless, the iron oxide catalysts, including ferrospinels, are more resistant to catalytic poisons. They are also cheaper and nonpolluting. It was shown, that magnetic microspheres of stabilized composition, isolated from ashes contain substantial part of iron in the form of a solid solution based on Fe_3O_4 or ferrospinels, therefore they can posses activity in the reactions of catalytic oxidation.

Catalytic activity of magnetic microspheres was tested both in the reactions of oxidative coupling and deep oxidation of methane. At high temperatures, the selectivity of formation of C_2H_6, C_2H_4 and CO from CH_4–O_2 feeds reaches 76–81 %, corresponding to characteristics of the best known catalysts of oxidative coupling of methane [5, 17]. Activity of the deep oxidation of methane (Fig. 5) was found to be lower than that for pure α-Fe_2O_3 ((4–8) 10^{16} *vs.* 31.5 10^{16} molecules $CH_4/(s\ m^2)$, correspondingly; 500 °C, $CH_4 : O_2 = 2 : 98$), but of the same order of magnitude as for magnesium ferrite $MgFe_2O_4$ (3.2 10^{16} molecules $CH_4/(s\ m^2)$) [13, 14].

At present time, the quantitative composition of (Ca,Mg,Al,Mn)-ferrites, being the active component of microspheres, is not established. Nevertheless, taking into account that formation of ferrospinels takes place from ferrosilicate melts, it can be presumed that (Ca,Mg)-ferrite content in the composition of solid solution is determined by the total content of calcium and magnesium. As it follows from Fig. 5, microspheres with (CaO + MgO) content of 5–8 % mass display the highest catalytic oxidation activity. This phenomenon is likely to be caused by the peculiarities of active component formation.

CONCLUSION

The processes of separation of microspheres from fly ash and their possible applications for the creation of catalytic supports, adsorbents and catalysts have been reviewed. To isolate magnetic microspheres and cenospheres of stabilized composition, the process flowsheets of concentrate separation, based on the combination of hydro- or aerodynamic and granulometric classification, followed by the separation in magnetic field of different intensity, were developed. Novel materials based on cenospheres of stabilized composition, such as mesoporous microspherical glasses (specific surface area $S_{sp} = 3-50$ m^2/g), the supported iron oxide systems ($S_{sp} = 50-200$ m^2/g), and zeolites are described. Spherical zeolites demonstrated good ion exchange properties of in cesium and strontium removal from the technological solutions The Fe_2O_3/cenosphere catalysts have been tested in the reaction of methane deep oxidation, and magnetic microspheres – in the reactions of methane oxidative coupling and deep oxidation, and the catalyst compositions displaying the highest activities have been established.

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