Physicochemical and catalytic properties of glass crystal catalysts for the oxidation of methane

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Abstract

Magnetic microspheres and cenospheres recovered from fuel ashes were studied by SEM, XRD, electron probe microanalysis, chemical analysis and Mössbauer spectroscopy. The magnetic microspheres were shown to consist of a crystal phase based on a solid solution of Fe_3O_4–Mg, Mn, Ca-ferrite, α-Fe_2O_3 and a glass phase composed of calcium ferrite, fayalite, wollastonite, ferrous olivines and mullite. The morphology of globules and size of crystallites of active phase were established to depend on the basicity of the glass phase. It was shown that catalytic activity of magnetic microspheres and cenospheres in oxidative conversion of methane is determined by component containing iron and depends on its accessibility and distribution on the surface. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The complicated oxide systems with spinel and perovskite structures are promising as the catalysts for the high-temperature (973–1473 K) processes because of their catalytic activity and thermal stability [1,2]. Among them are the novel microspherical catalysts with the certain composition, which were separated from the coal and lignite fly ashes. The catalysts obtained consist of the active crystal phase and glass phase. The active phase of this type of catalysts includes the solid solution of Fe, Ca, Mg, Mn-ferrites and α-Fe_2O_3. The glass phase of different compositions fulfils the role of a binding matrix material. It was shown that these catalysts can exhibit a good performance in the reactions of methane oxidation [3].

The objective of the present paper is to study in detail the composition and structure of the massive microspheres and cenospheres by modern physicochemical methods as well as their catalytic behaviour in the reactions of both the deep oxidation and oxidative coupling of methane.

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2. Experimental

A novel type of catalysts on the base of glass crystal microspheres and cenospheres was produced as a result of Kuznetskii coal (series P) and Irsha–Borodinskii lignite (series K) combustion following magnetic separation and hydrodynamic classification of fly ash [4]. The products recovered contain 98% magnetic fraction. In addition to magnetic separation, cenospheres have been separated by gravitation method using organic liquids (ethanol and hexane). To elucidate the role and structure of the active phase, the cenospheres were treated with 6N HCl at 90–100°C for 1 h resulting to the increase of the specific surface up to 3.2 m^2/g compared to the initial value 0.3 m^2/g.

The catalysts obtained were studied by different methods: XRD, SEM, Mössbauer spectroscopy, chemical analysis and electron probe microanalysis. The detailed description of the analysis technique was given in the previous works [3–5].

Catalytic properties of microspheres were studied in a microcatalytic setup with a quartz reactor loaded with 0.3 g of the catalyst. The flow-rate of the reaction mixture ($CH_4:O_2:He = 30:15:55$ vol.%) was 0.1–0.5 ml/s. The catalysts were preliminarily exposed to a standard treatment by an oxygen flow at 823 K for 1 h. The composition of the product stream was analysed by chromatograph ''Biochrom-1'' using thermal conductivity and flame ionisation detectors. The rates of products formation in deep oxidation were determined under steady-state conditions for the oxygen conversions of less than 5%.

3. Results and discussion

3.1. Formation of the magnetic microspheres in coal combustion

Conditions of formation of the magnetic microspheres determine their physicochemical and catalytic properties. Because of this, to study the mineral forms of the chemical element, localization in the magnetic microspheres as well as specific features of their formation in the thermochemical conversion of iron constituents of coals was of interest. The different coal basins vary from each other by the mineral forms of iron. Iron is distributed uniformly between aluminosilicates, pirite and carbonates in coals of the Kuznetskii basin. As for coals of the Kansk–Achinsk basin, the significant part of iron occurs in the form of complex humates, while the content of aluminosilicate and carbonate forms of iron is low [6].

In spite of variety of mineral forms of iron in coals, almost all of them take part in formation of magnetic microspheres [7]. An obvious correlation between the content of the magnetic microspheres in fly ash and the content of iron in coals characterized by different mineral forms of this element is an evidence of the total mobilization of iron.

The ferrous (Fe^{2+}) silicate melts containing the additional metal cations (Ca, Al, Mg, Mn) is the most probable form of the iron mobilization. The formation of the magnetic microspheres proceeds in a wide range of compositions of low-temperature eutectics (1366–1473 K) for a ternary system $CaO–SiO_2–FeO$ [8]. The mechanism of the iron accumulation in the silicate melts depends directly on acidity–basicity of melts, initial valence of iron and composition of a gas phase. As the oxidative potential of the system increases and the melt is cooled, the solubility of iron decreases. This effect is accompanied by the crystallization of iron oxides and the polymerization of a residual silicate melt forming the magnetic microspheres.

3.2. Composition and morphology of the magnetic microspheres and cenospheres

It was shown that there are two morphological types of globules including massive and hollow microspheres [3]. The content of hollow microspheres is 50–60% for P series and 10–

15% for K series. The cenospheres are the hollow microspheres with a shell of 5–10 μm in thickness.

The compositions of the glass phase in the magnetic microspheres were classified according to its basicity modulus $M_b = (CaO + MgO)/(SiO_2 + Al_2O_3)$ depending on a ratio of acidic and basic oxides (Table 1). It was established that the common feature of the glass phase of hollow globules compared to massive ones is an enhanced content of an acidic component Al_2O_3 and a reduced content of a basic component CaO. This fact causes the decrease of the basicity modulus from 0.4–0.8 (massive microspheres) to 0.2 (hollow microspheres of K and P series). The cenospheres are characterized by the least basicity modulus equal to 0.05.

Apart from the fact that the hollow and massive microspheres are constituted by glass of different compositions, they correspond to various types of eutectics. The polished cross-sections of individual globules display that the coarse crystalline structure is characteristic for the massive microspheres (Fig. 1a), while the hollow and porous microspheres are fine crystalline dendrite formations (Fig. 1b). The fine crystalline structure of a cenosphere shell (Fig. 1c) is distinctly displayed after an HCl etching (Fig. 1d).

The established connection between the morphology of globules, crystalline structure and the basicity of the glass phase shows that the morphology of the globules and the crystalline structure are a direct consequence of the initial melt composition at the step of microsphere formation. The basic melts are highly mobile and fluid so gas inclusions formed at thermal dissociation of minerals can easily escape from the melt. This fact explains a low content of the hollow microspheres in magnetic products of fuel ashes formed from lignite (series K 10–15%). Amount of the hollow microspheres in magnetic products of coal ashes formed from acidic melts is 50–60% (series P). In this case, the gas bubble is not able to escape from viscous acidic glass. The cenospheres are formed from ultra-acidic melts of high viscosity, which are poorly crystallized and vitrified at cooling.

As the total chemical analysis shows, the main component of the magnetic microspheres is iron. The iron content in K and P microspheres recalculated for Fe_2O_3 ranges from 83 to 88 wt.%. An exception is the cenospheres containing only 4–8 wt.% Fe_2O_3.

Using data of the Mössbauer spectroscopy, XRD and electron probe microanalysis, it was established that the solid solution of magnetite with impurities of Mg, Ca and Mn-ferrites is the dominant constituent of the crystal phases for the K and P magnetic microspheres independent of the globule morphology. The second crystal phase is hematite α-Fe_2O_3, its amount being 5–20 wt.% of a spinel content. The glass phase of magnetic microspheres corresponds to compositions of calcium ferrite, fayalite, wollastonite and ferrous olivines.

The dominant constituent of the cenospheres is an amorphous glass phase containing fine inclusions of the crystal spinel phase with crystallites being less than 2 mm. The amount of hematite in the cenospheres is very low and does not exceed 10 wt.% of the spinel phase. The glass phase of the cenospheres corresponds to the composition of mullite.

As the data of the Mössbauer spectroscopy indicate (Table 2), the dominant iron-containing phase for the magnetic microspheres of K and P

Table 1
Average chemical compositions (wt.%) and basicity modulus (M_b) of glass phase of magnetic microspheres and cenospheres 0.1–0.16 mm according to data of electron probe microanalysis

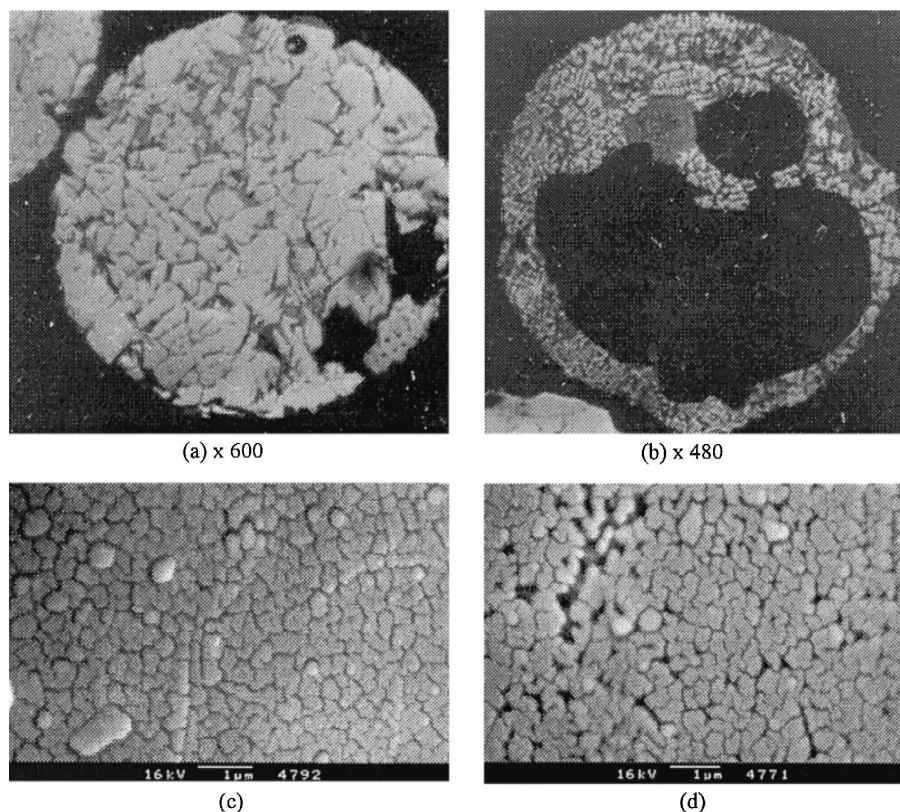| Type of morphology	SiO$_2$	Al$_2$O$_3$	MgO	CaO	FeO	MnO	P$_2$O$_5$	Σ	M_o
Microspheres of K series									
Massive	28.7	1.2	1.1	22.7	39.2	0.9	0.3	94.1	0.8
Hollow	30.5	16.5	1.7	6.0	44.4	–	0.1	99.2	0.2
Microspheres of P series									
Massive	32.8	9.0	5.2	10.4	28.9	1.7	0.4	88.4	0.4
Hollow	32.2	12.6	6.0	3.7	38.8	1.1	0.1	94.5	0.2
Cenospheres									
Hollow	62.3	19.9	2.3	1.5	5.9	0.1	0.2	92.2	0.05

Fig. 1. Polished cross-sections of the magnetic microspheres of different morphology 0.1–0.16 mm (a,b) and the surface of the initial cenospheres (c) and the cenospheres after the HCl etching (d) 0.1–0.16 mm with the bulk density 0.52 g/cm^3.

series, which formed from basic and acidic melts, is a crystal phase: hematite and solid solution of magnetite and Mg, Ca and Mn-ferrites (94–98 at.%). For the cenospheres, the ultra-acidic melts leads to the formation of high content of paramagnetic iron containing a glass phase (54–61 at.%) identified as Fe^{2+}-mullite and Fe^{3+} (6- and 4- coordinated)–iron silicate [9].

The complex characterization of the magnetic microspheres and the cenospheres performed by modern physicochemical methods has shown that the composition of an active component containing iron is the same for all catalysts. The cenospheres differ from the magnetic microspheres by the morphology, fine crystal structure of the surface (Fig. 1) and the total content of the active component. Because of this, the comparison of catalytic properties of the magnetic microspheres and the cenospheres in test reactions of the methane oxidation was of interest.

3.3. Catalytic properties of the magnetic microspheres and cenospheres in reactions of the oxidative conversion of methane

Catalytic properties of the K and P magnetic microspheres in reactions of deep oxidation and oxidative condensation of methane (mixture $CH_4 : O_2 = 85 : 15$ vol.%) were studied earlier [3]. The action of the magnetic microspheres in oxidative condensation of methane was found to be determined by the spinel phase from Fe, Ca, Mg and Mn-ferrite being defective on Fe^{2+}. The increase of the Fe^{2+} concentration in the spinel

Table 2
Data of Mössbauer spectroscopy of magnetic microspheres and cenospheres 0.1–0.16 mm
δ — isomer shift relative to natural iron, ± 0.02 mm/s; H — superfine field, ± 5 KOe; ε — quadrupole splitting, ± 0.02 mm/s; S — the assignment of iron to the certain phase or crystallographic position, ± 0.03.

| Simple	δ	H	ε	S	Assignment	
Series K	0.39	518	−0.34	0.08		α-Fe_2O_3
	0.32	493	0.02	0.48	$Fe^{3+a}_{(A+B)}$	
	0.58	461	−0.01	0.27	$(Fe^{2+} + Fe^{3+})_B$	
	0.61	423	0.13	0.11		
	0.21	0	0.74	0.06	Fe^{3+} (4)	glass silicate
Series P	0.39	515	−0.31	0.05		α-Fe_2O_3
	0.32	490	0.04	0.48	$Fe^{3+}_{(A+B)}$	
	0.57	458	−0.03	0.29	$(Fe^{2+} + Fe^{3+})_B$	
	0.69	421	0	0.12		
	0.25	0	0.40	0.04	Fe^{3+} (4)	glass silicate
	0.49	0	1.75	0.01	Fe^{3+} (6)	glass silicate
Cenospheres with bulk density 0.52 g/sm³	0.49	467	0	0.34	Fe^{3+}	spinel phase
	0.65	401	0.12	0.12	Fe^{2+}	
	1.06	0	2.02	0.28	Fe^{2+}-	mullite
	0.45	0	1.14	0.18	Fe^{3+} (6)-	glass silicate
	0.28	0	0	0.08	Fe^{3+} (4)-	glass silicate

[a](A) — tetrahedral position, (B) — octahedral position of spinel phase (Ca, Mg, Mn-ferrites and magnetite).

phase causes the linear increase of selectivity of C_2-products formation. The activity of the magnetic microspheres in deep oxidation of methane depends on the properties of two phases such as hematite and spinel.

Catalytic properties of the separated cenospheres of different densities and sizes in the deep oxidation of methane ($T = 773$ K, mixture $CH_4:O_2:He = 30:15:55$ vol.%) are displayed in Fig. 2. It can be seen that the cenospheres of density 0.52 g/cm³ are the most active in the reaction, the rate of the deep oxidation being larger by a factor of 4–13 than that for the cenospheres of the same size but less density. It can be suggested that the increased catalytic activity is due to concentrating of crystallographically formed homogeneous magnetite in heavy products (magnetite density 5.2 g/cm³) as a result of a gravitation separation.

The treatment of the cenospheres of density 0.52 g/cm³ with the HCl acid causes a decrease of the deep oxidation rate by a factor of 17 compared to the initial catalysts. This effect takes place due to a leaching of the active spinel

phase. Residual iron (about 4.5 wt.%) is referred to the catalytic inert glass phase containing iron such as mullite and iron silicate. The
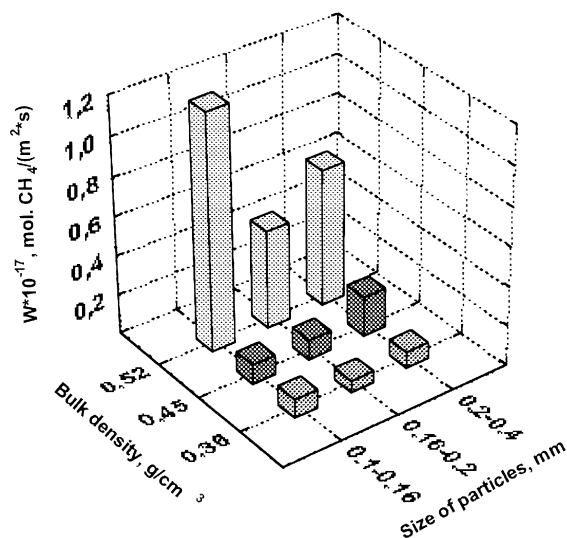
Fig. 2. The rate of the deep oxidation of methane at 773 K over the cenospheres ($CH_4:O_2:He = 30:15:55$ vol.%).

structure of the cenosphere surface displayed after the HCl etching demonstrates that the content of the active component does not exceed 30% of the total sphere surface (Fig. 1d).

The comparison of catalytic properties of the cenospheres and the magnetic microspheres P 0.1–0.16 in deep oxidation of methane ($T = 773$ K, mixture CH_4:O_2:He = 30:15:55 vol.%) was carried out. The rate of deep oxidation for P 0.1–0.16 calculated for the total specific surface of the catalyst was 8.2×10^{16} CH_4 molecules/(m^2 s). This value is less than for the cenospheres of density 0.52 g/cm^3 and size 0.1–0.16 mm by a factor of 1.5 (Fig. 2). The rates of the deep oxidation calculated for the iron content in the active component were 7.6×10^{14} CH_4 molecules/(g$_{Fe}$ s) and 1.5×10^{16} CH_4 molecules/(g$_{Fe}$ s), respectively. As for the cenospheres, the active component is distributed on the globule surface and completely accessible causing the high activity of the catalysts in deep oxidation compared to the magnetic microspheres. The main part of the active phase in the magnetic microspheres is beyond reach of reagents.

In spite of the fact that the catalytic activity of the cenospheres in the deep oxidation of methane depends on their density and size to a great extent, in the oxidative condensation of methane ($T = 1123$ K, mixture CH_4:O_2:He = 30:15:55 vol.%, the degree of O_2 conversion is 12%), all catalysts are characterized by the close values of selectivities of C_2-hydrocarbon and carbon oxides formation (%): C_2 — 33–38, CO — 41–46, CO_2 — 19–24. This fact is likely to correlate with the alteration of phase composition in the catalysts resulting from the change of redox conditions at high temperatures. It can be believed that the spinel phase is oxidized forming α-Fe$_2$O$_3$. The total selectivity of the C_2-hydrocarbon and carbon monoxide formation over the cenospheres ranges from 76% to 81%.

4. Conclusions

The magnetic microspheres and cenospheres were shown to consist of the crystal phase based on a solid solution of Fe_3O_4–Mg, Mn, Ca-ferrite and α-Fe$_2$O$_3$ as well as a glass phase composed of calcium ferrite, fayalite, wollastonite, ferrous olivines and mullite.

The correlation between the globule morphology, size of the crystallites of the active phase and the basicity modulus of the glass phase for the magnetic microspheres and the cenospheres was established. It was shown that the globule morphology is caused by the composition of an initial melt.

The catalytic activity of the magnetic microspheres and the cenospheres in both the deep oxidation and oxidative coupling of methane is determined by a component containing iron and depends on its accessibility and distribution on the surface of the spheres.

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