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Novel glass crystal catalysts for the processes of methane oxidation

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Abstract

Novel catalysts were prepared from magnetic microspheres and cenospheres recovered from fuel ashes being formed in combustion of Irsha-Borodinskii lignite and Kuznetskii coal. The specific features of microsphere formation in the coal combustion were discussed. The morphology as well as composition of different magnetic microspheres and cenospheres were studied by SEM, electron probe microanalysis and Mössbauer spectroscopy. The morphology of globules, crystallite size and defect structure of active phase was established to depend on the basicity of the glass phase. It was shown that catalytic activity of magnetic microspheres and cenospheres in the reaction of deep oxidation of methane is determined by the spinel phase and depends on the extent of its accessibility and type of defect structure. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Magnetic microspheres; Cenosphere; Morphology; Basicity modulus; Methane; Deep oxidation

1. Introduction

Complicated oxide systems with spinel and perovskite structures are promising as catalysts for high temperature (973–1473 K) processes because of their catalytic activity and thermal stability [1,2]. Among there are the novel microspherical catalysts with the specific composition which were separated from the coal and lignite fly ashes by magnetic separation and following hydrodynamic classification [3]. 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 is composed of calcium ferrite, fayalite, wollastonite, olivines and mullite [4]. The action of magnetic microspheres in oxidative coupling of methane (mixture CH_4:O_2 = 85:15 vol.%, $T = 1123$ K) was found to be determined by the spinel phase $(Me_a{}^{2+}Fe_{x+b}{}^{3+})[Fe_x{}^{2+}Fe_{1+a}{}^{3+}Me_b{}^{2+}]O_4$ (Me = Ca, Mn and Mg) being defective on Fe^{2+}. The increase of the Fe^{2+} concentration in the spinel phase results in a linear increase of selectivity of C_2-products formation. The activity of the magnetic microspheres in deep oxidation of methane at 793 K depends on the properties of two phases such as hematite and spinel. However, the influence of globule morphology, the size of crystallites and their defect structure on the catalytic properties of magnetic microspheres is still

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unclear. In particular, the accessibility of the spinel active phase for reagents has not been studied for microspheres of different morphology.

The objective of the present paper is to study the influence of the composition of the magnetic microspheres on the globule morphology, size and defect structure of spinel crystallites and catalytic properties in the reaction of deep oxidation of methane.

2. Experimental

A novel type of catalysts on the base of glass crystal microspheres and cenospheres was produced as a result of coal (P series) and lignite (K series) combustion followed by magnetic separation and hydrodynamic classification of fly ash [3]. 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). Magnetic microspheres (K and P series) of 0.1–0.16 mm as well as cenospheres of 0.1–0.16, 0.16–0.2, 0.2–0.4 mm and different bulk density were under investigation.

To establish dimensions of ferrite spinel inclusions in cenospheres they were treated with 6 N HCl at 363–373 K for 1 h. The treatment resulted in the increase of the specific surface area 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: SEM, Mössbauer spectroscopy, electron probe microanalysis. Detailed description of the analysis technique was given in the previous works [3–5].

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

3. Results and discussion

3.1. Formation of novel glass crystal catalysts and their characteristics

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 lignite of the Kansk–Achinsk basin, the significant part of iron occurs in the form of complex humates, the content of aluminosilicate and carbonate forms of iron being low [6]. In spite of variety of mineral forms of iron in coals, almost all of them take part in the formation of magnetic microspheres. The obvious correlation between the content of magnetic microspheres in fly ash and the content of iron in coals ($K = 0.97$) characterised by different mineral forms of this element is the evidence of total mobilisation of iron [7]. The ferrous (Fe^{2+}) silicate melts containing the additional metal cations (Ca, Al, Mg, Mn) is the most probable form of iron mobilisation. The formation of this melt in coal combustion 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 iron accumulation in the silicate melts directly depends on acidity–basicity of melts, initial valence of iron and composition of 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 crystallisation of a ferrosilicate melt to form a ferrite spinel and polymerisation of a residual silicate melt forming the magnetic microspheres. It is just this stage which is responsible for the formation of the globule porous structure and crystallites of the spinel phase determining the properties of the novel catalytic systems in oxidative conversion of methane.

The size of the spinel crystallites, the morphology and variations of composition for individual globules of cenospheres as well as massive and porous microspheres (0.1–0.16 mm) were determined by SEM and electron probe microanalysis. The analysis of SEM images for the microspheres has shown that there are two morphological types of globules including massive (Figs. 1a and 2a) and porous (Figs. 1b and 2b) ones. It should be noted that K series contains 85–90%

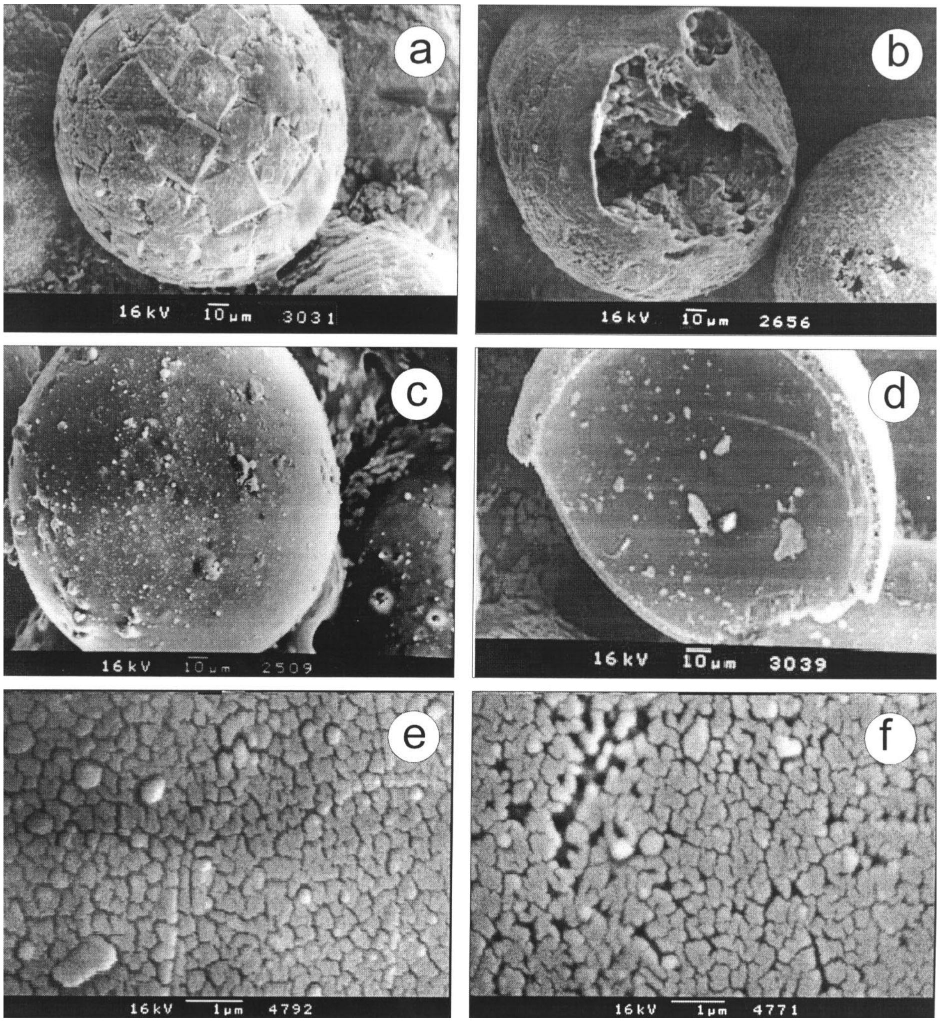

Fig. 1. Magnetic microspheres 0.1–0.16 mm of K and P series: (a) massive; (b) porous; (c, d) cenospheres 0.1–0.16 mm; (e) the surface of initial cenospheres; (f) the surface of cenospheres after HCl etching.

massive globules, whereas the content of the same ones in P series is 40–55% (Figs. 1a and 2a). Cenospheres are the hollow microspheres with a shell of 5–10 μm in thickness (Fig. 1c and d). The distinctions between different types of globule morphology is likely to be resulted from the different compositions of ferrosilicate melt formed in combustion of coals and lignite.

To elucidate the influence of initial melt composition on the globule morphology the individual massive and porous globules (K and P series) were studied by the electron probe microanalysis. Taking into account that microspheres contain both CaO, MgO, SiO_2, Al_2O_3 and iron oxides, the data obtained are presented as a ternary diagram $(CaO + MgO)–(SiO_2 + Al_2O_3)–FeO$ (Figs. 3 and 4). For massive microspheres of K series some compositions fall on an FeO–calcium silicate line and cover a wide field of the diagram corresponding to the composition of olivine (Fig. 3). The other compositions are located in the field of ferromontichellite $CaFeSiO_4$, calcium ferrites including monocalcium ferrite $CaFeO_2$ and semicalcium ferrite $CaFe_2O_4$ and fayalite $2FeO{\cdot}SiO_2$.

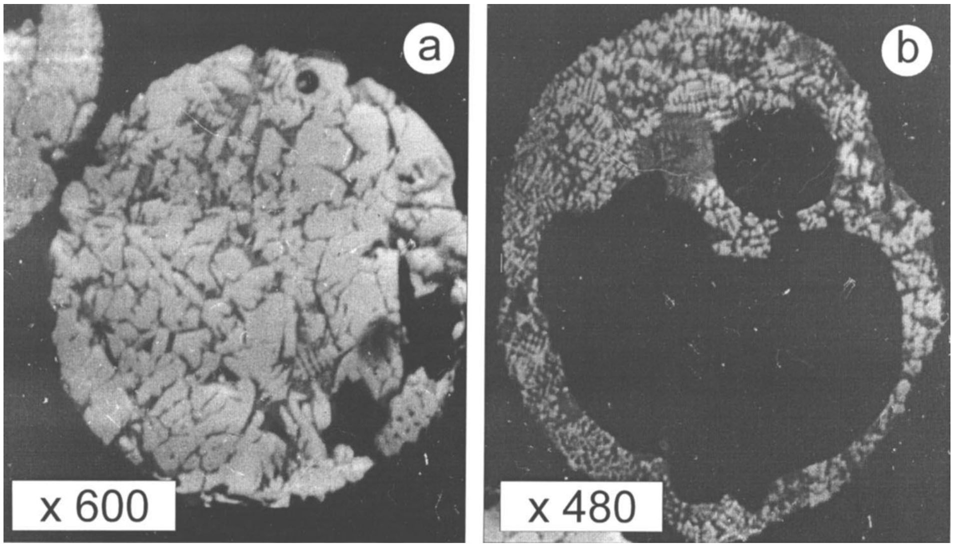

Fig. 2. Polished cross-sections of magnetic microspheres 0.1–0.16 mm of different morphology: (a) massive; (b) porous.

Another trend of crystallisation which is characteristic for porous microspheres is in the more acidic field of wollastonite (Fig. 4). The silicate binder of the P magnetic microspheres is also in the field of olivine as in the case of K microspheres. There are some compositions of porous globules in the field of calcium ferrites and close to fayalite $2FeO \cdot SiO_2$.

Based on the study of the individual globules of magnetic microspheres, it can be concluded that dif-

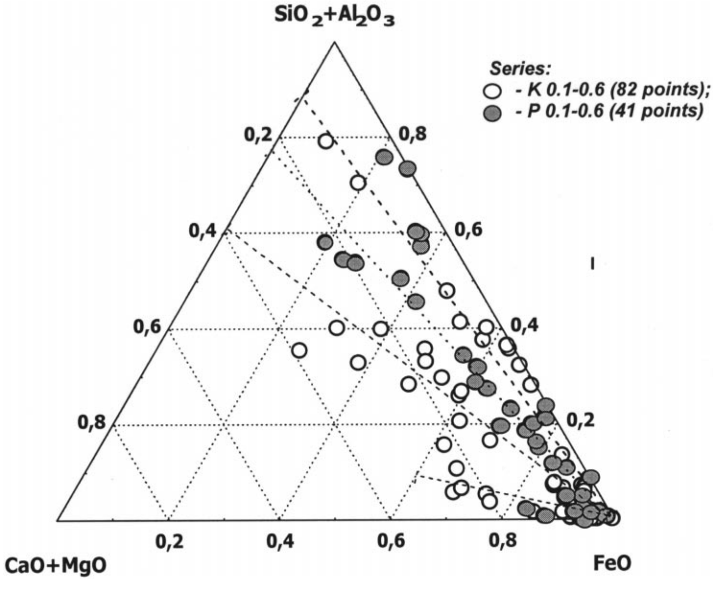

Fig. 3. Chemical composition (wt.%) of massive magnetic microspheres of K and P series 0.1–0.16 mm in the limits of a ternary diagram $(CaO + MgO)$–$(SiO_2 + Al_2O_3)$–FeO.

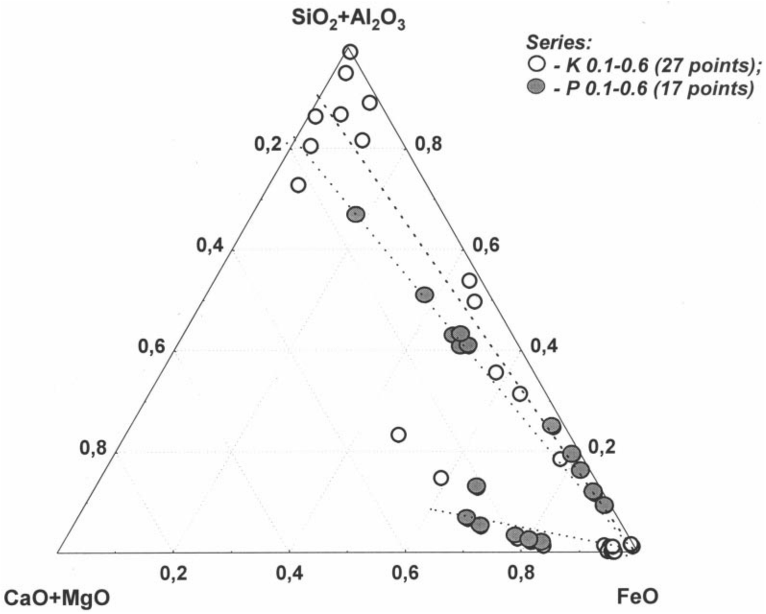

Fig. 4. Chemical composition (wt.%) of porous magnetic microspheres of K and P series 0.1–0.16 mm in the limits of a ternary diagram $(CaO + MgO)–(SiO_2 + Al_2O_3)–FeO$.

ferent morphology types of microspheres are arisen from the melts of different composition. The attempt to describe reasons responsible for formation of certain structural features which are important in catalysis will be made below.

3.2. The influence of composition on the morphology of globules, crystallite size and defect structure

From the data of the electron probe microanalysis, compositions of the glass phase in 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. It was established that the common feature of the glass phase of porous 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 0.8 (massive microspheres) to 0.2 (porous microspheres) for K and P series. Cenospheres are characterised by the least basicity modulus equal to 0.05 (Table 1).

Apart from the fact that cenospheres and massive microspheres are constituted by glass of different composition, they correspond to various types of eutectics. The basic melts are more mobile for gas inclusions

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	Content (%)	SiO_2	Al_2O_3	MgO	CaO	FeO	MnO	P_2O_5	Σ	M_b
Microspheres of K series										
Massive	85–90	28.7	1.2	1.1	22.7	39.2	0.9	0.3	94.1	0.8
Porous	10–15	30.5	16.5	1.7	6.0	44.4	–	0.1	99.2	0.2
Microspheres of P series										
Porous	50–60	32.2	12.6	6.0	3.7	38.8	1.1	0.1	94.5	0.2
Cenospheres										
Hollow	98–100	62.3	19.9	2.3	1.5	5.9	0.1	0.2	92.2	0.05

formed at thermal dissociation of minerals to be able to easily escape from the melt. This fact explains a low content (10–15%) of porous microspheres in magnetic products of fuel ashes formed from lignite (K series). Amount of porous microspheres in magnetic products of coal ashes formed from acidic melts is 50–60% (P series). In this case the gas bubble is not able to escape from viscous acidic glass. The polished cross-sections of individual globules display that the coarse crystalline structure of spinel phase is characteristic for massive microspheres (Fig. 2a), but porous microspheres are fine crystalline dendrite formations (Fig. 2b). The fine crystalline structure of a cenosphere shell is distinctly displayed only after HCl etching (Fig. 1e and f). Sizes of spinel phase crystallites determined from SEM images are 10–50 μm for K series and 2–5 μm for P series. Cenospheres are formed from ultra acidic melts of high viscosity which are poorly crystallised and vitrified at cooling, the dimension of ferrite phase inclusions in a cenosphere shell being in the range 0.1–0.3 μm.

The Mössbauer spectrum of magnetic microspheres is superposition of several subspectra for different non-equivalent iron positions (Fig. 5). The parameter

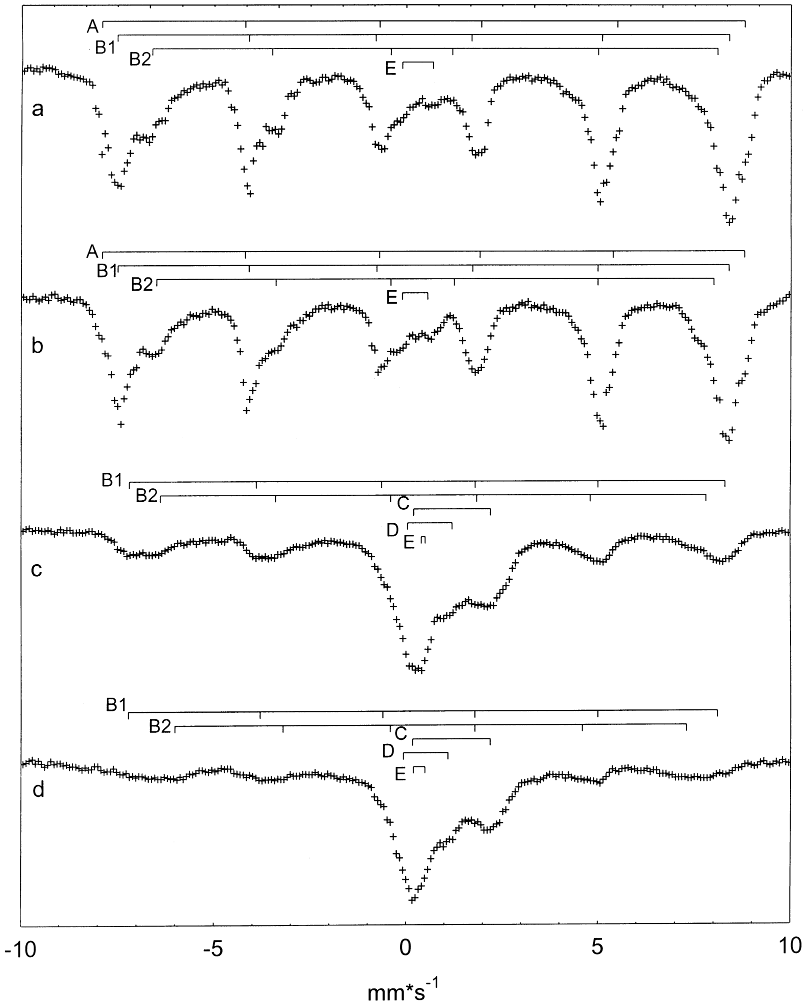

Fig. 5. Mössbauer spectra of magnetic microspheres and cenospheres: (a) K series 0.1–0.16 mm; (b) P series 0.1–0.16 mm; (c) cenospheres 0.1–0.16 mm of 0.52 g/cm^3; (d) cenospheres 0.1–0.16 mm of 0.52 g/cm^3 after HCl etching. The assignment of A, B1, B2, C, D and E to the iron valence or position is marked in Table 2.

Table 2
Mössbauer parameters of initial magnetic microspheres and initial cenospheres (0.1–0.16 mm)[a]

Sample	δ	H	ε	W	S			Assignment
K series	0.39	518	−0.34	0.25	0.08	(A)	Fe^{3+}	α-Fe_2O_3
	0.32	493	0.00	0.52	0.45	(B1)	Fe^{3+}	Spinel phase
	0.58	457	0.00	0.87	0.41	(B2)	$Fe^{2.5+}$	Spinel phase
	0.14	0	0.84	0.83	0.06	(E)	Fe^{3+} (4)	Glass silicate
P series	0.38	515	−0.29	0.25	0.05	(A)	Fe^{3+}	α-Fe_2O_3
	0.32	489	−0.04	0.52	0.47	(B1)	Fe^{3+}	Spinel phase
	0.59	450	−0.04	0.96	0.42	(B2)	$Fe^{2.5+}$	Spinel phase
	0.09	0	0.65	0.62	0.06	(E)	Fe^{3+} (4)	Glass silicate
Cenospheres of 0.52 g/cm^3	0.42	479	−0.02	0.65	0.13	(B1)	Fe^{3+}	Spinel phase
	0.55	440	−0.05	1.34	0.32	(B2)	$Fe^{2.5+}$	Spinel phase
	1.04	0	2.05	0.98	0.28	(C)	Fe^{2+}	Mullite
	0.45	0	1.12	0.82	0.20	(D)	Fe^{3+} (6)	Glass silicate
	0.29	0	0.05	0.60	0.07	(E)	Fe^{3+} (4)	Glass silicate
Cenospheres of 0.52 g/cm^3 after HCl etching	0.39	472	−0.20	0.73	0.08	(B1)	Fe^{3+}	Spinel phase
	0.51	413	−0.16	1.51	0.25	(B2)	$Fe^{2.5+}$	Spinel phase
	1.03	0	2.02	0.98	0.34	(C)	Fe^{2+}	Mullite
	0.36	0	1.14	0.86	0.26	(D)	Fe^{3+} (6)	Glass silicate
	0.21	0	0.34	0.36	0.07	(E)	Fe^{3+} (4)	Glass silicate

[a] δ: isomer shift relative to natural iron, ±0.02 mm/s; H: hyperfine field, ±5 kOe; ε: quadrupole splitting, ±0.04 mm/s; W: width of spectral lines; S: occupation of the certain phase or crystallographic position by iron, ±0.03; $Fe^{2.5+}$: iron in a state of a mixed valence arisen from fast electronic exchange between ions of Fe^{2+} and Fe^{3+} in octahedral positions of magnetite.

values of subspectrum hyperfine structure allow to identify the valence state of iron and its assignment to specific phase (Table 2). The study of the temperature influence on Mössbauer spectra has shown that the relation of magnetic and paramagnetic phases of cenospheres is not changed up to the temperature of liquid nitrogen. This fact points to the presence of paramagnetic compounds of iron identified as Fe^{2+}-mullite and Fe^{3+} (6- and 4-coordinated)-iron silicate [9].

The initial samples of K and P series are characterised by the similar values of ratio of iron phases and Mössbauer parameters of the spinel phase $(Me_a{}^{2+}Fe_{x+b}{}^{3+})[Fe_x{}^{2+}Fe_{1+a}{}^{3+}Me_b{}^{2+}]O_4$ (Me = Ca, Mg, Mn). Moreover, the spinel phase of microspheres of P series is more disordered. This is evidenced by the more wide spectral lines and reduced values of hyperfine fields.

As it can be calculated from the data of Table 2 for K and P series, the ratio of the area of sextet (B1) to that of sextet (B2) (see caption of Fig. 5 for a definition of these sextets) is significantly different from this ratio for stoichiometric magnetite ($\frac{2.2}{2}$, $\frac{2.24}{2}$ for K and P series, respectively, and $\frac{1}{2}$ for stoichiometric magnetite). The observed excess of Fe^{3+} in the spinel phase cannot be explained only by formation of Mg, Mn-ferrites because their content in the crystal phase is low. It is likely that the most part of octahedral iron cations in magnetite does not take part in the electronic exchange due to distortion of the crystal lattice and/or presence of cation and anion vacancies. The most probable reason of the Fe^{3+} excess is the cation vacancies in the magnetite structure. Consequently, the spinel phase should be divided not into magnetite and ferrite but into two magnetite phases including the ideal phase with the electronic exchange and phase with defect structure without exchange.

The hematite amount in initial cenospheres is beyond the detection limit with the spinel content being lower than in K and P series. Comparing to the K and P series, the B1/B2 ratio being equal to $\frac{0.81}{2}$ deviates from the ideal value in the opposite direction. This fact testifies that the spinel phase is characterised by an excess of Fe^{2+} and/or oxygen vacancies. The content of oxygen vacancies in cenospheres is lower than the content of cation vacancies in K and P series. At the same time the hyperfine fields on the

Table 3
Characteristics of samples and their specific catalytic activity in the reaction of deep oxidation of methane ($T = 773\,K$, CH_4:O_2:He = 30:15:55 vol.%)

Sample	Size of particles (mm)	Bulk weight (g/cm^3)	Surface area (BET) (m^2/g)	Total content of Fe (wt.%)	Content of Fe in spinel phase (wt.%)	$W \times 10^{16}$ (CH_4 molecules/m^2 s)
Cenospheres	0.2–0.4	0.36	0.4	4.8		0.8
	0.2–0.4	0.45	0.3	4.6		1.6
	0.2–0.4	0.52	0.4	5.2		6.6
	0.16–0.2	0.36	0.4	4.7		0.6
	0.16–0.2	0.45	0.3	5.2		1.0
	0.16–0.2	0.52	0.3	5.2		4.8
	0.1–0.16	0.36	0.4	4.9	3.1	1.0
	0.1–0.16	0.45	0.3	5.4	2.9	1.1
	0.1–0.16	0.52	0.3	5.7	2.6	11.9
Cenospheres after HCl etching	0.1–0.16	0.52	3.2	4.5	1.5	0.5
P series	0.1–0.16	1.8	0.5	57.7	35.2	15.4
K series	0.1–0.16	2.3	0.3	61.2	34.9	10.1
α-Fe_2O_3	<0.05	–	0.4	69.9	–	27.0

iron nuclei of the spinel phase are noticeably less than in K and P series but spectral lines are substantially widened. These data indicate that the spinel phase in the cenospheres is the more heterogeneous than in the microspheres. The isomer shifts are enhanced, respectively, K and P series due to the decrease of an electron density on the iron nuclei. The heterogeneity of the spinel phase is accompanied by expansion of the lattice.

The complex characterisation of magnetic microspheres and cenospheres performed by modern physicochemical methods has shown that the morphology of globules, crystallite size and defect structure of a catalytic active component (ferrite spinel) depend strongly on the modulus of basicity of the glass phase of magnetic microspheres. Because of this, the comparison of catalytic properties of magnetic microspheres and cenospheres in reaction of deep oxidation of methane was of interest.

3.3. *Catalytic properties of magnetic microspheres and cenospheres in reactions of deep oxidation of methane*

Catalytic properties of ferrites $MeFe_2O_4$ (Me = Mg, Mn, Co, Ni, Cu, Zn, Cd), Fe_2O_3 and Fe_3O_4 in the reaction of methane oxidation were studied in detail earlier at 623–808 K using gradientless reactor [10,11]. It was shown that differences of the ferrite activity are in the range of one order of magnitude, α-Fe_2O_3 being the most active among the catalysts studied. Under reaction conditions iron ferrite (Fe_3O_4) transforms to α-Fe_2O_3 which determines catalytic properties. The similar conversion of ferrite spinel into α-Fe_2O_3 was established by authors for magnetic microspheres of K series in the reaction of oxidative coupling of methane [12].

The properties of cenospheres of different bulk weight and microspheres of K and P series as well as the activity of α-Fe_2O_3 are presented in Table 3. In spite of the fact that the microspheres of K and P series have the similar high contents of the defect spinel phase, their specific activity differs by a factor of 1.5 (Table 3). The more readily accessible active phase for components of a gas phase can be the reason of the enhanced activity of microspheres of P series which are characterised by the increased porosity of globules and less sizes of crystallites. It should be noticed that the activity values of both the spinel phases and α-Fe_2O_3 are in a good agreement with results presented in [10,11].

The content of total iron and the spinel phase in cenospheres is smaller approximately by a factor of 10 as in microspheres of K and P series (Table 3). In accordance with the results of the Mössbauer study (Table 2, Fig. 5) the defect structures of spinels are strongly distinguished and characterised by the oxygen deficiency in the case of cenospheres of 0.1–0.16 mm. The growth of the specific activity with the increase of the globule density is observed for all fractions of cenospheres. The specific activity of cenospheres of 0.1–0.16 mm is raised by one order of magnitude as the content of the spinel phase decreases (Table 3). It can be explained by the different accessibility of the active spinel phase for components of the reaction.

To clarify the question the more active cenospheres (0.1–0.16 mm, 0.52 g/cm^3) were etched with hydrochloric acid. The etching of the cenospheres caused the decrease of the reaction rate by a factor of 20 in deep methane oxidation with the specific surface of cenospheres increasing by one order of magnitude. This fact can be an evidence of the almost complete elimination of the accessible active component (Table 3). Alternatively, cenospheres after HCl etching save magnetic properties pointing to the presence of the spinel phase inaccessible for HCl. As Mössbauer data indicate (Table 2), only content of spinel iron decreases (from 2.6 to 1.5 wt.%) after HCl treatment of cenospheres. At the same time the content of iron associated with mullite and iron silicate does not change. Only 42% of the spinel phase is accessible, whereas 58% is encapsulated in glass and remains inaccessible for HCl and reaction mixture. Hence the differences of the catalytic activity for cenospheres of distinct densities can be explained by different extent of accessibility of the defect spinel phase.

The SEM images of the cenosphere surface after HCl etching demonstrate that the coverage of the sphere surface with the active phase does not exceed 15–30% (Fig. 1f). The rate of deep oxidation calculated for the surface of active component became equal to 4×10^{17}–8×10^{17} CH_4 molecules/m^2 s. Such enhanced specific catalytic activity of cenospheres compared to microspheres of K and P series is likely to be caused by the high concentration of oxygen vacancies in the defect spinel phase of cenospheres. However, to make the unambiguous conclusions the detailed study of the accessible surface of the active component and the nature of defect structure is required.

4. Conclusions

1. Correspondence between the globule morphology, crystallite size of the ferrite spinel and the basicity modulus of the glass phase for magnetic microspheres and cenospheres was established.
2. The defect spinel phase of magnetic microspheres is characterised by the excess of Fe^{3+} but the spinel phase of cenospheres contain in excess Fe^{2+} and/or oxygen vacancies.
3. The catalytic activity of magnetic microspheres and cenospheres in deep oxidation of methane depends on the extent of accessibility of the defect spinel phase.

Acknowledgements

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References

[1] T. Seima, Catal. Rev.-Sci. Eng. 34 (4) (1992) 281.

[2] Z. Zhong, K. Chen, Y. Ji, Q. Yan, Appl. Catal. A 156 (1997) 29.

[3] A.G. Anshits, V.A. Nizov, E.V. Kondranenko, E.V. Fomenko, N.N. Anshits, A.M. Kovalev, O.A. Bajukov, O.M. Sharonova, A.N. Salanov, Chem. Sustainable Dev. 7 (1999) 105.

[4] E.V. Fomenko, E.V. Kondranenko, A.N. Salanov, O.A. Bajukov, A.A. Talyshev, N.G. Maksimov, V.A. Nizov, A.G. Anshits, Catal. Today 42 (1998) 267.

[5] A.G. Anshits, E.V. Voskresenskaya, E.V. Kondranenko, E.V. Fomenko, E.V. Sokol, Catal. Today 42 (1998) 197.

[6] M.Ya. Shpirt, V.P. Kler, I.Z. Pertsikov. Inorganic Components of Solid Fuels, Chimia, 1990, p. 240.

[7] L.Ya. Kizilshtein, I.V. Dubov, A.L. Shpitsgluz, S.P. Parada, The Components of Ashes and Slags of Power Plants, Energoatomizdat, Moscow, 1995, p. 176.

[8] T.Ya. Malysheva. Iron-Ore Sources: Strengthening by Heat Treatment, Metallurgie, 1988, p.199.

[9] L.C. Ram, P.S.M. Tripathi, S.P. Mishra, Fuel Process. Technol. 42 (1995) 47.

[10] G.K. Boreskov, V.V. Popovskii, N.E. Lebedeva, V.A. Sazonov, T.V. Andrushkevitch, Kinet. Katal. 11 (1970) 1253.

[11] G.K. Boreskov, V.V. Popovskii, N.E. Lebedeva, V.A. Sazonov, T.V. Andrushkevitch, Kinet. Katal. 12 (1971) 979.

[12] E.V. Fomenko, E.V. Kondratenko, O.M. Sharonova, V.P. Plekanov, S.V. Koshcheev, A.I. Boronin, A.N. Salanov, O.A. Bajukov, A.G. Anshits, Catal. Today 42 (1998) 273.