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Novel microdesign of oxidation catalysts. Part 1. Glass crystal microspheres as new catalysts for the oxidative conversion of methane

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Abstract

New catalysts designed as glass crystal microspheres were obtained as a result of coal and lignite combustion, hydrodynamic classification of fly ash followed by magnetic separation. The physicochemical and catalytic properties of three different systems of new catalysts were studied by SEM, XRD and Mossbauer spectroscopy. The active component of the new systems was shown to include α-Fe_2O_3 and a solid solution formed from magnetite and Mg(Mn)-ferrite. High-temperature eutectics (1473–1673 K) on the base of calcium aluminosilicates are represented as a matrix material. The growth of the Fe^{2+} concentration in the spinel phase results in increase of selectivity of C_2-product formation in oxidative coupling of methane at 1123 K and in a decrease of catalytic activity of deep oxidation at 793 K. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Oxidative coupling; Deep oxidation; Microspheres; Ferriferrous oxides

1. Introduction

For the last ten years a new generation of high-temperature catalysts is being developed for treating automotive exhaust gases, CO_2+CH_4, CH_4+H_2O reactions and oxidative conversion of C_1–C_2 hydrocarbons. An intensive heat and mass transfer as well as stability of regular macroporous structure (1–100 microns) at high temperature (up to 1473 K) in oxidative and reducing conditions are important properties of this kind of catalysts.

The analysis of the literature shows that both the catalysts for deep oxidation [1] and the catalysts for oxidative dehydrogenation of olefins [2] can be prepared on the basis of ferriferrous oxides and ferrites. Moreover, an outgrowth of the concept of catalytic action of structural defects in oxidative coupling of methane [3–5] gives rise to the preparation of systems on the base of iron which – depending on the composition of reaction mixture and temperature – have different defect structures and energies of the metal–oxygen bond.

The objective of the present work is to study the active component composition of the iron-containing catalysts designed as glass crystal microspheres by

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SEM, XRD, Mossbauer spectroscopy and their catalytic performance in the reactions of deep oxidation and oxidative coupling of methane.

2. Experimental

Three different systems of new catalysts (K, P and T) designed as glass crystal microspheres were obtained as a result of coal and lignite combustion, hydrodynamic classification of fly ash followed by magnetic separation [6].

The study of the grain-size distribution of obtained catalysts indicates (Fig. 1) that 50% of the particles of K system are as large as 1–5 μm. The P system is characterized by a wide maximum of distribution being in the range 10–100 μm (76% of the particles). The maximum of the grain-size distribution for the T system is observed in the range 100–400 μm (86% of the particles).

To study catalytic properties the narrow fraction of catalysts <0.05 and 0.16–0.1 mm were drawn off.

The catalyst K<0.05 contains 75% of particles of 1–5 μm in diameter, 85% of particles P<0.05 are massive microspheres of 10–50 μm in diameter with different levels of glassy solidification. Calcium aluminosilicates of different composition are represented as a binding matrix material.

The catalysts K 0.16–0.1 and P 0.16–0.1 are of the same design, 85–90% of active phase being in the form of dendrite structures (Fig. 2). The catalysts differ in proportions of matrix material (10% and 14%, respectively) and the content of spheres with a hollow structure filled with small particles of 1–10 μm in diameter. The content of hollow microspheres is 50% for P 0.16–0.1 and 15% for K 0.16–0.1.

The T system consists of hollow microspheres with a shell of 5–10 μm in thickness (Fig. 3). The content of the active phase is 20%. Calcium aluminosilicate $CaO\cdot Al_2O_3\cdot 2SiO_2$ is a binding material.

Catalytic properties of the glass crystal microspheres were studied in a microcatalytic set-up with a quartz reactor with 0.1–0.3 g of the catalyst. The flow-rate of the reaction mixture (CH_4:O_2=85:15 vol%) was 0.2–0.3 ml/s.

Preliminarily the catalysts were exposed to a standard treatment by an oxygen flow at 823 K for 1 h. The catalysts were quenched in a helium flow after catalytic experiments at 1123 K. The composition of the product stream was analyzed by chromatograph "Biochrom-1" using thermal conductivity and flame ionization detectors. The rates of formation of products of deep oxidation were determined under steady-state condition for oxygen conversions of less than 5%. The BET method was utilized to determine the surface areas of the catalysts.

The phase composition was evaluated by the XRD method applying a X-ray diffractometer DRON-3 (Cu K_α irradiation).

Mossbauer studies were carried out at room temperature applying a NTA-1024 spectrometer with a Co^{57} (Cr) source. The assignment of iron to a defined

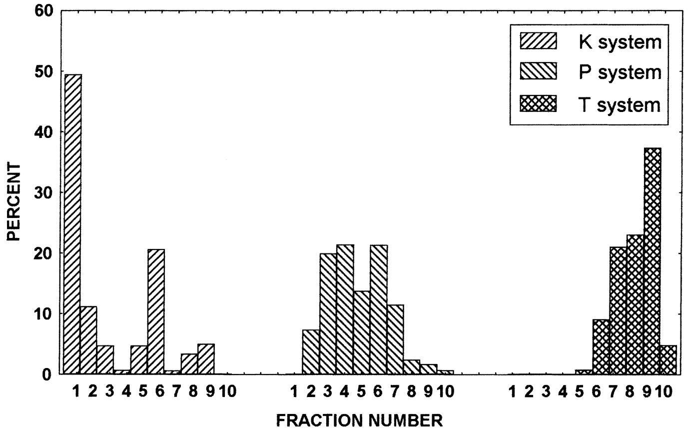

Fig. 1. Grain-size distribution of glass crystal microspheres: (1) 1–5; (2) 5–10; (3) 10–20; (4) 20–50; (5) 50–63; (6) 63–100; (7) 100–160; (8) 160–200; (9) 200–400; (10) 400–1000 microns.

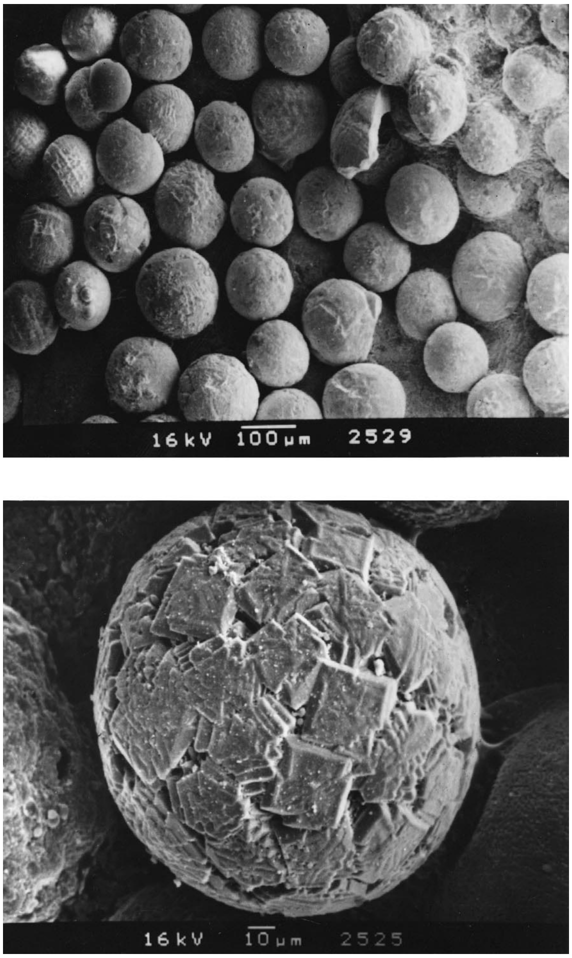

Fig. 2. Glass crystal microspheres K and P 0.16–0.1.

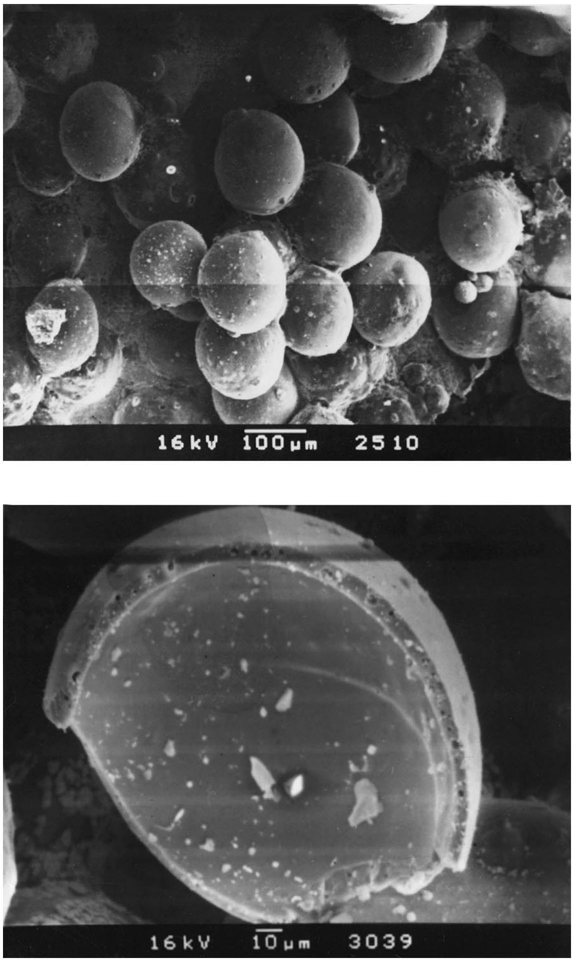

Fig. 3. Glass crystal microspheres T 0.16–0.1.

phase or crystallographic position was obtained from reference data [7].

The morphology of the catalysts was studied by using a scanning electron microscope (SEM) BS-350, "Tesla".

3. Results and discussion

The physico-chemical and catalytic properties of three systems of glass crystal microspheres in deep oxidation of methane are presented in Table 1. As XRD and Mossbauer spectroscopy data indicate the catalysts differ in composition of active phase and size of crystallite particles of the spinel phase. The data presented in Table 1 show that different systems of catalysts are characterized by different values of the activation energy in deep oxidation in a temperature range from 630 to 960 K. The difference in values of the activation energy may be caused by concentration of Mg and Mn ions in the spinel phase and their location in tetrahedral or octahedral positions.

The strength of metal–oxygen bond depends on the symmetry of neighbour surrounding. In particular, the relationship between catalytic properties and structure of neighbour surrounding for complicated catalysts with spinel structure was investigated in [8]. It was found that octahedral Co ions are characterized by small energy of bond Me–O and thus a high catalytic activity in the reaction of deep oxidation. The location

Table 1
Composition of active phase and catalytic properties of glass crystal microspheres in deep oxidation of methane (conversion of O_2 <5%, $CH_4:O_2=85:15$ vol%)

Type and size of glass crystal microspheres (mm)	S_{BET} (m^2/g)	Composition of active phase for initial catalysts (wt%)		Average crystallite size of the spinel phase (Å)	Value of (x) for [Fe^{2+}] in the spinel phase	Deep oxidation at 793 K $W\times10^{-17}$, molec.CH_4/m^2 s	E_a (kJ/mol)
		α-Fe_2O_3	Spinel phase				
K<0.05	0.5	11.7	79.7	>1000	0.51	5.3	107
K 0.16–0.1	0.3	6.9	82.8	qq550	0.58	2.8	81
K 0.16–0.1 after treatment with HF [10]	1.4				0.64	0.6	137
P<0.05	0.5	13.6	76.3	400	0.46	6.5	119
P 0.16–0.1	0.5	4.1	82.2	450	0.54	4.8	74
T 0.16–0.1	0.7	1.8	7.9+10.3PM[a]	260	0.47	1.4	84

[a] PM – paramagnetic state.

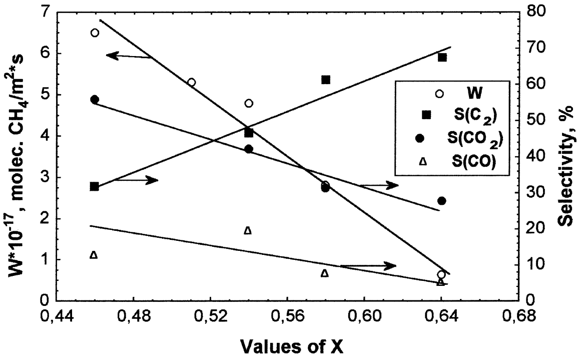

Fig. 4. Effect of Fe^{2+} content (X) in spinel phase of $(Me_a^{2+}Fe_{x+b}^{3+})[Fe_x^{2+}Fe_{1+a}^{3+}Me_b^{2+}]O_4$ on the selectivity of OCM-product formation (at 1123 K) and activity of deep oxidation (at 793 K) over glass crystal microspheres (CH_4:O_2=85:15 vol%).

of Co ions in tetrahedral positions leads to stabilization of Co (II) state. In this case the low activity in the reaction of deep oxidation is due to the availability of strong bonded oxygen. The dependence of the catalyst activity on the composition of the spinel phase was also observed in [9] for Fe–Ni catalysts used in the oxidative dehydrogenation of olefins at 653 K.

The content of Fe^{2+} in the spinel phase $(Me_a^{2+}Fe_{x+b}^{3+})[Fe_x^{2+}Fe_{1+a}^{3+}Me_b^{2+}]O_4$ was evaluated by Mossbauer spectroscopy. The dependences of catalytic activity in the deep oxidation of methane at 793 K and the selectivities of product formation in the oxidative coupling of methane at 1123 K as a function of Fe^{2+} content in the spinel phase are presented in Fig. 4. The data obtained for catalyst K 0.16–0.1 after treatment with HF [10] follow the same dependence because of stabilization of iron in its Fe^{2+} state as will be shown in Part II. It can be seen from Fig. 4, that the growth of Fe^{2+} concentration in the spinel phase results in an increase in the selectivity of C_2-product formation. At the same time, the selectivity for formation of carbon oxides in oxidative coupling of methane decreases and the rate of deep oxidation reduces linearly.

Unlike the K and P systems, the catalysts of the T 0.16–0.1 system do not follow the dependence mentioned above. The following values of selectivity of product formation (in %) were obtained for T 0.16–0.1 system in oxidative coupling of methane: $C_2 - 41$, CO_2 – 16 and CO – 43. The difference of microdesign (hollow microspheres, Fig. 3), high contents of the glass phase (80%) and the iron containing phase being in the paramagnetic state (57%) result in a sufficiently high selectivity of CO formation in the oxidative coupling of methane.

Thus, the study of the catalytic activity of the new systems designed as glass crystal microspheres showed that catalysts obtained are active in the reactions of deep oxidation and oxidative coupling of methane depending on the composition of active phase and type of design. A dependence of the rate of CO_2 formation in deep oxidation and the selectivity of formation of C_2-products, CO and CO_2 in the oxidative coupling of methane on the content of Fe^{2+} in the spinal phase was observed.

4. Conclusions

1. New efficient catalysts on the base of glass crystal microspheres were obtained as a result of coal and lignite combustion, hydrodynamic classification followed by magnetic separation. The active phase of the catalysts includes α-Fe_2O_3 and solid solution of Fe_3O_4 and Mg(Mn)-ferrite. The high temperature eutectics of calcium aluminosilicates with different composition are used as a binding matrix material.
2. It was established that the growth of Fe^{2+} concentration in the spinel phase results in the increase of selectivity of C_2-product formation. At the same time, the selectivity of formation of carbon oxides in oxidative coupling of methane at 1123 K decreases, the rate of deep oxidation reduces linearly at 793 K.

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