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Catalysis Today 42 (1998) 273–277

CATALYSIS TODAY

Novel microdesign of oxidation catalysts. Part 2. The influence of fluorination on the catalytic properties of glass crystal microspheres

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Abstract

New catalysts designed as glass crystal microspheres were studied by XPS, SEM, XRD and Mossbauer spectroscopy. The data obtained indicated that after treatment of catalysts with HF the fluorination of lattice took place leading to stabilization of Fe_3O_4 phase. The catalytic activity of initial catalysts and catalysts already treated with HF in the reactions of deep oxidation and oxidative coupling of methane was determined. The yield of C_2-products at 1123 K was 16% for oxyfluoride systems using the gas mixture CH_4:O_2=85:15 vol%. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Methane; Oxidative coupling; Deep oxidation; Microspheres; Fluorination

1. Introduction

The catalytic performance of metal oxide catalysts for oxidative coupling of methane can be effectively promoted by metal fluoride [1,2]. It was shown [3] that oxyfluorides MOF (M=rare earth metal) were formed in some catalysts.

It was of interest to study the influence of fluorination on the catalytic properties of new catalysts designed as glass crystal microspheres [4].

The aim of the present work is to study the active component composition of initial catalysts designed as glass crystal microspheres and catalysts after treatment with HF by XPS, SEM, XRD, Mossbauer spectroscopy and their catalytic performance in the reactions of deep oxidation and oxidative coupling of methane.

2. Experimental

The catalytic testing, process equipment, preparation technique of catalyst and their characterization data were described in Part 1.

X-ray photoelectron spectra (XPS) were recorded with the aid of electron spectrometer VG ESCALAB by Fisons Instruments (Great Britain). Al K_α line ($h\nu$=1486.6 eV) was used for the electron excitation. The spectral resolution, which can be characterized by full width at half maximum (fwhm) of the $Ag_3d_{5/2}$ line, was 1.3 eV. The calibration of the line position was made relatively Cls line with E_b=284.8 eV from

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PII S0920-5861(98)00102-3

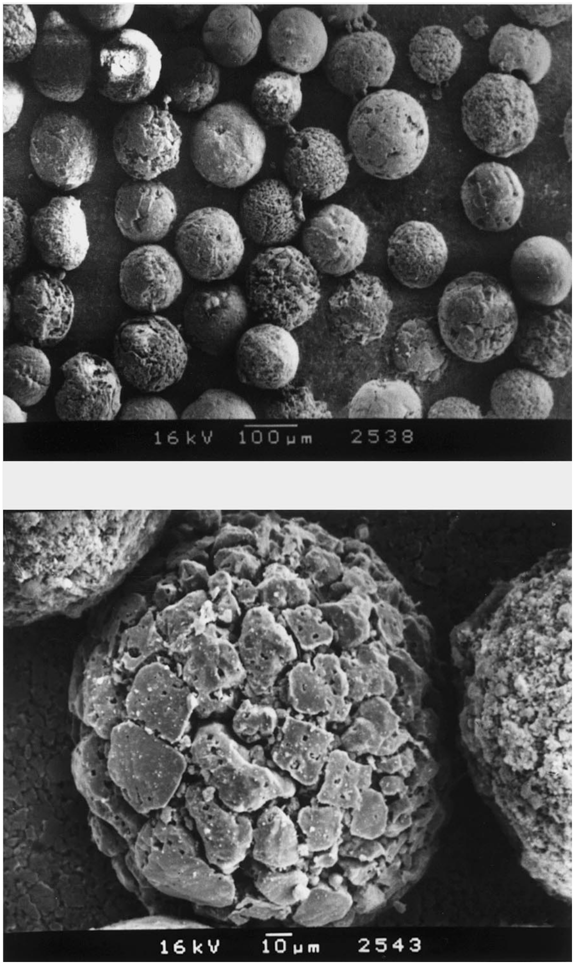

Fig. 1. Glass crystal microspheres K 0.16 – 0.1 after treatment with HF.

carbon contaminations on the sample surface. The curve fitting procedure was performed by Gaussians after the background subtraction based on Shierly's approach with the aid of the original CALC program [5].

Treatment of catalyst K 0.16–0.1 with HF (5 ml HF per 1 g catalyst) causes etching of the glass phase along the boundary of an active component block (Fig. 1). The specific surface of this catalyst after treatment with HF is 1.4 m^2/g.

3. Results and discussion

The study of the new types of catalysts in deep oxidation of methane showed that the $P<0.05$ system is more active in the temperature range from 630 to 960 K (Fig. 2) with CO_2 formation rate being greater compared to the catalyst K 0.16–0.1 system. The Arrhenius relation for $P<0.05$ evaluated per active component approximates to the same relation for Fe_2O_3 and Fe_3O_4. The inflection at the Arrhenius curve for Fe_3O_4 at 530 K is connected with the change of the reaction from an associative oxidation mechanism of methane to a stepwise (redox) one and the change of activation energy from 27 to 116 kJ/mol. Earlier [6] the related inflections at the Arrhenius plot were obtained for the oxidation of CO on Fe_2O_3 with an activation energy in the temperature range 430–590 K equal to 109 kJ/mol. The close value of the E_a of a stepwise oxidation mechanism equal to 119 kJ/mol was obtained for $P<0.05$.

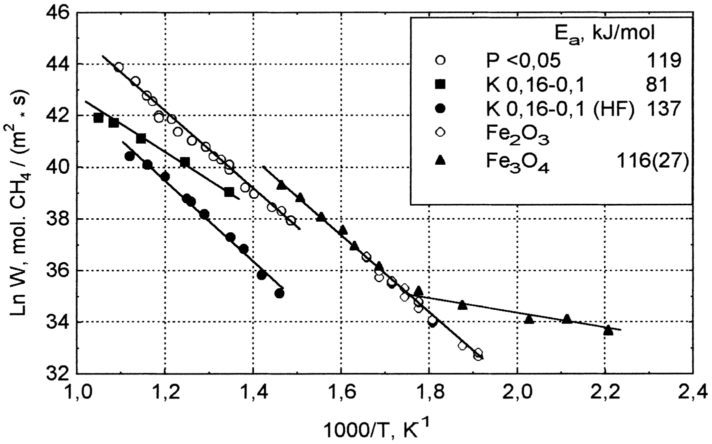

Fig. 2. Arrhenius relation of catalytic activity of glass crystal microspheres (CH_4:O_2=85:15 vol%).

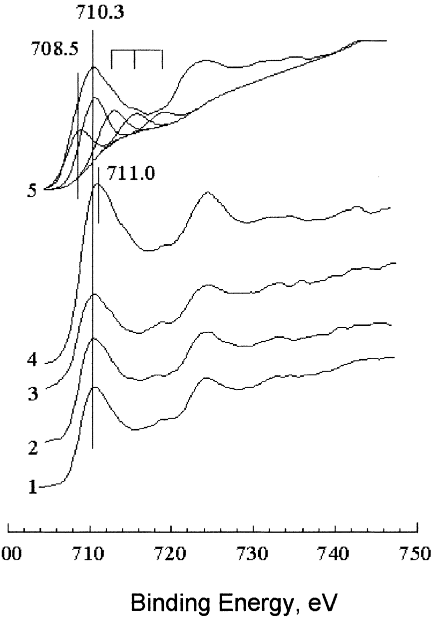

Fig. 3. Fe2p binding energy spectra of catalysts: (1) P<0.05, (2) K 0.16–0.1, (3) K 0.16–0.1 after catalysis, (4) K 0.16–0.1 after treatment with HF, (5) K 0.16–0.1 after treatment with HF and after catalysis.

Using the Mossbauer spectroscopy data it was established that the treatment of K 0.16–0.1 with HF causes a change in composition of the active component. The decrease of superfine field values from 430 to 415 kO points to the fact that substitution of O^{2-} for F^- and Mg^{2+} for Fe^{2+} occurs in a spinel phase [7].

As XPS data indicate fluorination results in the growth of the intensity of Fe2p line and its shift to the side of more high binding energies (Fig. 3, curve 4). It is obvious that the increase in intensity is bounded with the etching of silicate phase covering the iron oxides. The comparison with the reference data [5,8,9] allows to make a certain conclusion that this Fe state cannot be related with the FeF_3 phase but formally can be interpreted as a FeF_2. However, taking into account that fluorination cannot reduce the oxides, but rather the substitution of oxygen by fluorine takes the place, we can reliably interpret spectrum 4 in Fig. 3 as the oxifluoride state of Fe^{3+}.

Formation of oxyfluorine systems results in a lower catalytic activity of K 0.16–0.1 after treatment with HF in deep oxidation of methane.

The catalytic activity of the catalysts obtained was also determined in the oxidative coupling of methane. The catalysts were tested before and after reaction by Mossbauer spectroscopy and XPS (Table 1).

For catalyst P<0.05 the selectivity of formation of C_2-products, CO_2 and CO at CH_4 conversion 18.3% amounted up to 32%, 56% and 12%, respectively. The peculiarity of catalyst K 0.16–0.1 is the increase of selectivity of C_2-product formation up to 61% with the selectivity of CO_2 and CO formation being equal to 32% and 7%, respectively. In this case the conversion of methane was 15.5%. The treatment of catalyst K 0.16–0.1 with HF causes the growth of selectivity of C_2-product formation up to 67% and conversion of methane up to 23.8%.

As it was mentioned above fluorination of catalyst K 0.16–0.1 with HF results in the formation of oxyfluorine complexes. It was determined that an active component of unfluorinated and fluorinated K 0.16–0.1 systems after catalytic reaction and cooling in helium flow is of variable composition. The variation in phase composition of an active component was found by Mossbauer spectroscopy and XPS. As indicated in Table 1 a considerable part of a spinel phase in K 0.16–0.1 was oxidized to α-Fe_2O_3 as a result of catalysis. It is known [10] that at $P_{O_2}<0.1$ kPa ferrite spinel is partially reduced and decomposed into MgO and FeO followed by oxidation of wustite to hematite.

The active component of catalyst K 0.16–0.1 HF after catalysis is a solid solution of magnetite with a trace impurity of Mg(Mn)-ferrite. On evidence of XPS the shoulder from the low binding energy side appears in Fe2p spectrum (Fig. 3, curve 5). Thus, this shoulder can be clearly displayed as one of the components of the complicated original spectrum in the result of the curve fitting procedure. This shoulder can evidence about the appearance of Fe^{2+} state of iron. In this case α-Fe_2O_3 is reduced forming magnetite. The spinel phase is also reduced followed by decomposition of the spinel phase into FeO and MgO. But in this case incorporation of fluorine ions into the spinel lattice and formation of oxyfluorine complexes during catalysis stabilize iron in its Fe^{2+} state and prevent its oxidation up to α-Fe_2O_3.

Thus, the study of catalytic properties and phase composition of new catalytic systems designed as glass crystal microspheres showed that the change

Table 1

Composition of active phase from data of Mossbauer spectroscopy and catalytic properties of catalysts for oxidative coupling of methane (CH_4:O_2=85:15 vol%)

Type and size of glass crystal microspheres (mm)	Content of iron in active phase for initial catalysts (at.%)			Oxidative coupling of methane at 1123 K				Content of iron in active phase after catalysis and cooling in helium flow (at.%)		
	Fe_2O_3	Fe_3O_4	Mg(Mn) Fe_2O_4	Conversion of CH_4 (%)	Selectivity (%)			Fe_2O_3	Fe_3O_4	Mg(Mn) Fe_2O_4
					C_2	CO_2	CO			
P<0.05	17	47	36	18.3	32	56	12			
K 0.16–0.1	8	61	31	15.5	61	32	7	60	36	4
K 0.16–0.1 after treatment with HF	14	57, 3PM[a]	25	23.8	67	28	5	—	93	7

[a] PM – superparamagnetic state.

of activity and selectivity in methane oxidation can be related with the change of iron state and in consequence the change of oxygen state. Fluorination of these systems substantially changes the chemical composition of the surface and positively effects on a stability of an active component in Fe_3O_4 phase due to the formation of oxifluoride complexes preventing the oxidation of Fe^{2+}.

4. Conclusions

1. New catalysts for the oxidative conversion of methane on the basis of glass crystal microspheres were designed. It was found that the obtaining catalysts can be active in the reaction of deep oxidation and oxidative coupling of methane depending on the composition of reaction mixture and reaction temperature,
2. Catalytic performance of the catalysts obtained depends on the design level and state of iron and oxygen. Fluorination of the system results in the formation of oxyfluoride complexes stabilizing iron in its Fe^{2+} state and preventing magnetite from being oxidized.

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