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Catalytic combustion of methane on substituted strontium ferrites

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ABSTRACT

Sr–hexaferrites prepared by co-precipitation method and calcined at 700–1000 °C have been characterized by thermogravimetric and differential thermal analysis (TG–DTA), Fourier transformed infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), hydrogen temperature-programmed reduction (H_2-TPR), and Ar adsorption techniques. It has been shown that hexaferrite phase formed after calcination at 700 °C is amorphous and its crystallization occurs at 800 °C. Specific surface area (S_{BET}) of the samples calcined at 700 °C is 30–60 m^2/g. Reduction in hydrogen proceeds in several steps, Fe(III) in the hexaferrite structure being practically reduced to Fe^0. Amount of hydrogen necessary for the reduction of the samples decrease in the order: $SrMn_2Fe_{10}O_{19} > SrFe_{12}O_{19} > SrMn_6Fe_6O_{19} > SrMn_2Al_{10}O_{19}$. Surface composition of the ferrites differs from bulk. According to XPS data, the surface is enriched with strontium. Sr segregation is most probably explained by the formation of surface carbonates and hydroxocarbonates. The main components on the surface are in oxidized states: Mn^{3+} and Fe^{3+}. Maximum activity in the methane oxidation is achieved for the $SrMn_xFe_{12-x}O_{19}$ ($0 \leqslant x \leqslant 2$) catalysts. These samples are characterized by highest amount of the hexaferrite phase, which promotes change of oxidation state $Mn(Fe)^{3+} \leftrightarrow Mn(Fe)^{2+}$.

1. Introduction

At the present, unburned hydrocarbons, CO and NO_x are main air pollutants in the cities which are produced by a vast amount of gasoline and diesel internal combustion engine vehicles. One of the ways to resolve this ecological problem is to use alternative fuels such as methane or natural gas. However, a major drawback associated with its use is the emission of unburned methane, an effective greenhouse gas which contributes to global atmosphere warming even more than CO_2 due to its longer lifetime [1]. Therefore, to comply with modern legislation, highly efficient catalysts for the complete abatement of unburned methane are needed.

Noble metal-based catalysts like Pt and/or Pd supported on mixed metal-oxides are typically employed for the oxidation of hydrocarbons [2]. Reducing the high cost of noble metal catalysts using inexpensive metals for the complete oxidation of hydrocarbons remains the major research target. Recently, it has been demonstrated that doped metal-oxides, perovskites, spinels, and other mixed metal-oxides are active for the methane oxidation [3]. Extremely high stability of methane compared to other hydrocarbons demands relatively high temperatures for the methane oxidation. Moreover, high exothermicity of this reaction: $CH_4 + 2O_2 = CO_2 + 2H_2O$ ($\Delta H_{298} = -802.7$ kJ/mol) [4] results in additional overheating of the catalysts applied for afterburning gas emissions in spite of low concentration of methane in exhaust feed. Therefore, the catalysts developed for the methane oxidation should be not only highly active, but also should be thermally stable in the temperature range of 800–1000 °C.

Recently it was shown [5,6] that substituted hexaaluminates can be applied for the methane oxidation. For Mn(Fe)-substituted hexaaluminates, which differ by nature of components and their ratio, the temperature (T_{50}) corresponding to 50% CH_4 conversion are in the range of 560–776 °C. The introduction of iron ions till total substitution of aluminum cations with iron ones and obtaining $BaFe_{12}O_{19}$ hexaferrite are accompanied by decrease of T_{50} to 533 °C [7]. It can be supposed that further T_{50} decrease can be achieved by using Mn-substituted hexaferrites.

The aim of this study was to synthesize substituted Sr–hexaferrites and to investigate the influence of nature and content of additive (Mn, Al) on their structure, chemical state of components, texture and catalytic performance in the methane oxidation.

2. Experimental

2.1. Catalyst preparation

Hexaferrites $SrMn_xFe_{12-x}O_{19}$ ($x = 0, 1, 2, 6$), $SrMn_6Fe_4Al_2O_{19}$ and $SrMn_2Al_{10}O_{19}$ marked as SF, SM1F, SM2F, SM6F, SM6FA2 and SM2A10, respectively, were prepared by co-precipitation of soluble

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nitrates of Sr, Fe and M (M = Mn(II), Al (III)) at pH = 7.2–7.5 and temperature of 70 °C with NH_4HCO_3 as a precipitating agent. The slurry was aged at 70 °C for 2 h and then filtered [8]. $SrMn_xFe_{12-x}O_{19}$ (x = 1, 2) samples marked as SM1F* and SM2F* were prepared in the same way. Difference is that hydrogen peroxide solution has been previously added to solution of Mn(II) nitrate for transformation of Mn(II) to Mn(III). The obtained precipitate was washed and dried in air. The solid was dried at 110 °C for 12–14 h and then calcined at 700 °C for 4 h in air flow. The subsequent calcination of the samples was carried out at 800 and 1000 °C for 4 h in a muffler. Except for the SM2A10 sample, the samples calcined at 700 °C were aged at 800 °C for 14 h in the 10% H_2O/air gas mixture.

2.2. Catalyst characterization

The catalysts were characterized using elemental analysis, Ar adsorption, thermogravimetric and differential thermal analysis, X-ray diffraction, Fourier transformed infrared spectroscopy, X-ray photoelectron spectroscopy, and hydrogen temperature-programmed reduction techniques.

Elemental analysis was performed using the ICP atomic absorption spectroscopy with an accuracy of 0.01–0.03% [9]. The specific surface area was determined with an accuracy of ±10% by the thermal desorption of argon [10].

The thermogravimetric and differential thermal analysis was carried out on a NETZSCH STA 449C apparatus. Catalysts were tested over the temperature range from room temperature up to 1200 °C at the heating rate of 10 °C/min in air. The accuracy of determination of weight losses was ±0.5%.

XRD studies were performed on a ARL X'TRA diffractometer using Cu $K\alpha$ monochromatic radiation (λ = 1.5418 Å). X-ray diffraction patterns were recorded in a step scan mode in the 2θ range from 10° to 75° with the step of 0.02–0.05° and 3–5 s per step depending on the sample crystallinity. The phase identification was performed by comparison of the measured set of the interplanar distances d_i and the corresponding intensities of the diffraction maximums I_i with that found in the ICDD, PDF-2.

Cell parameters of α-Fe_2O_3 (tetragonal structure) are calculated from equation:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2},$$

where, h, k, l are Miller Indices, d is interplanar distances, which is determined from the experiment. The corresponding number of the most accurate, not overlapping and quite intensive lines is selected for calculation of the cell parameters. It is desirable to select the lines in the region of large angles since at the same accuracy of determination of angles the accuracy of determination of interplanar distances increases. The least-squares method is employed for specification of the cell parameters that increases reliability of determination since all possible lines are used. The accuracy of determination of the cell parameters a and c is ±0.005 and ±0.01 Å, respectively.

FTIR spectra were recorded in the range of 250–2000 cm^{-1} on a Bomem MB-102 spectrometer. To take the spectra, the samples were prepared by the pelletizing with CsI.

X-ray photoelectron spectroscopy was applied for characterization of the surface contents of the elements. XPS measurements were performed on a SPECS's machine equipped with an X-ray source XR-50M with a twin Al/Ag anode, an ellipsoidal crystal monochromator FOCUS-500, and a hemispherical electron energy analyzer PHOIBOS-150. The core-level spectra were typically obtained using monochromatic Al $K\alpha$ radiation (h = 1486.74 eV) and fixed analyzer pass energy of 20 eV under ultrahigh vacuum conditions. During XPS measurements, the static charge was minimized by a flood gun of electrons. For further calibration of the charge shift, C*1s* peak at 284.8 eV from adventitious hydrocarbon was used. Spectra were background-subtracted using a Shirley fit algorithm [11] and then fitted onto separate components. Doniach–Sanjic symmetric function was applied for peak approximation [12]. To quantify the atomic concentration of the present elements, the cross-sections according to Scofield [13] were used.

H_2-TPR measurements were carried out in a flow reactor equipped with a thermal conductivity detector. The samples of 0.2 g with an average granule size of 0.25–0.5 mm were previously pretreated in oxygen at 500 °C for 30 min, and then they were cooled to room temperature. A 10 vol.% H_2/Ar stream (40 ml/min) was passed over the sample while it was heated from 40 to 900 °C at the heating rate of 10 °C/min.

2.3. Catalyst activity test

The catalyst activity in the methane oxidation was tested in accordance with temperature-programmed reaction (light-off test) in the temperature range from 100 to 625 °C at the heating rate of 10 °C/min using a mixture of 0.1 vol.% CH_4, 20 vol.% O_2, 0.5 vol.% Ne balanced with He at a total flow rate of 500 ml/min. Catalyst volume was 0.6 cm^3, space velocity was 50,000 h^{-1}. The gas composition was analyzed by a quadruple mass-spectrometer SRS QMS-200.

3. Results and discussion

3.1. Phase composition

Non-isothermal temperature-programmed treatments of the fresh air-dried samples resulted in the appearance of exo- and endoeffects on the TG–DTA curves (Fig. 1). When the precursors were heated from room temperature up to 1200 °C, they lost from 22% (SF) to 28% (SM6F) or even 36% (SM6FA2) of their weight. The endoeffects observed at 128–136 °C were caused by the dehydration of hexaferrites. The effects at 219–266 °C are probably related to the decomposition of ammonia salts of the corresponding components. According to [14], the endoeffects observed at 375–405 °C for the SM6F and SM6FA2 samples can be caused by the decomposition of iron carbonate. The endoeffects at 462–464 and 511–543 °C are related to the decomposition of manganese carbonate to MnO_2 followed by the transformation of MnO_2 to Mn_2O_3 [15,16]. The endoeffects at 840–856 °C are originated due to the decomposition of strontium carbonate [17]. The endoeffects at 980–995 °C can be related both to transition $Mn_2O_3 \rightarrow Mn_3O_4$ [16] and formation of spinel $(Mn_xFe_{1-x})_3O_4$ [18].

The exoeffects appears at 650–697 °C and 798 °C for the substituted and unsubstituted ferrites, respectively (Fig. 1). Exoeffect at 798 °C can be caused by crystallization of the $SrFe_{12}O_{19}$ phase, since $BaFe_{12}O_{19}$ crystallization occurs at 760 °C [19]. Probably, exoeffect at 650–697 °C is related to crystallization of Sr manganite. Thus, the thermal genesis of the ferrites exhibits the complex behavior pointing out the presence of the phase transformation.

XRD data (Figs. 2 and 3; Table 1) show that the samples calcined at 700 °C contain mainly $SrCO_3$ and α-Fe_2O_3 crystalline phases, whereas SM2A10 hexaaluminate system calcined at the same temperature is amorphous [20]. At the same time the SM6F and SM6FA2 samples contains also the Mn_2O_3 phase (Fig. 2c; Table 1) and the phases which were not identified. It should be stressed that the phase composition of the SM1F and SM1F* samples calcined at 700 °C depends on valence of manganese in the feedstock (Fig. 3a). The introduction of Mn(III) in the sample leads to