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COMPLEX ANALYSIS OF PHOSPHATE-BASED MATERIAL OXIDATION

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Abstract

The thermal stability of sample $Mo(PO_3)_3$ that is the initial material for novel catalysts for carbon monoxide oxidation has been studied. It has been concluded that molybdenum(III) methaphosphate is stable up to 435°C. Processes of partial oxidation and layering of specimens are determined. Novel material based on partial oxidized $Mo(PO_3)_3$ gives significant rise of the carbon oxidation rate. The molybdenum(III) metaphosphate is of a definite interest in view of its application in practice as initial material for new catalysts row formation with different content of $Mo(PO_3)_3$ and $MoOPO_4$ layers.

Keywords: carbon monoxide oxidation, catalyst, molybdenum(III) metaphosphate, thermal stability

Introduction

The last few decades have witnessed an increase of interest to the new phosphate-based materials as object for practical use in many fields of technology especially dealing with sorption and catalytic processes.

Compounds containing metal at low or mixed valence state usually used at selective or non-selective catalytic oxidation [1–3]. Their qualities at general are compared with best patterns of mixed oxide semiconductors. These compounds represent the first steps in the preparation of solid-state materials that would display a size or shape discriminatory adsorption into molecular sized micropores combined with a potentially catalytically active transition *d*-elements as covalently bonded part of the lattice within the micropores.

Different valence state of transition metal, dispersed at a solid matrix increases activities of the catalyst. The best way of different paramagnetic centre formation at matrix is partial oxidation of initial compound that contains the Mo^{3+}.

As new technological catalyst a series of differently substituted material $Mo(PO_3)_3$/$MoOPO_4$ have been analysed at CO oxidation.

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Experimental

The mixed catalyst specimens are obtained in two stages. At the first stage suspension consists of molybdenum dust (average participle size typically less than 15 nm) in 85% H_3PO_4 with components molar ratio of 3:1, which were placed in an alumina crucible and heated at 250°C to evaporated excess of water. All starting materials for synthesis were of analytical grade. Finally the resulted product was calcinated at 300°C (powder *A*). After cooling the resulting pale-yellow solid was dissolved in a large amount of hot water, and golden yellow powder of single phase was recovered by filtration. This phase was washed with acetone and dried in air by evaporation. At the second stage the mixed catalyst was synthesized by partial oxidation of *A* in temperature range from 400 up to 900°C for 10 h. During this treatment powder *A* transformed to powder *B*.

X-ray powder diffraction pattern was taken on a Philips diffractometer using CuK_α radiation with NaCl as internal standard. All observed peaks for *A* and *B* series can be indexed on the tetragonal cell for *A* and monoclinic cell for *B* given by Kierkegaard [1], Douglass and Staritsky [2] with the least-squares refined parameters: a=10.76, b=19.48, c=9.55 Å; β=97.6°; V=1984 Å^3 and also a=6.174, c=4.287 Å, V=163.4 Å^3.

Diffuse reflectance spectrum was registered at room temperature on a Specord M-40 spectrometer in the range of 10000–40000 cm^{-1}. Three broad absorption lines are observed and after Gauss curve plotted the maxima at 12000, 19100 and 25300 cm^{-1}. These lines are estimated to energy band transitions at $Mo^{5+}O_6$, which realized at complex in C_{4v} cite symmetry (*B*). Two broad cast absorption lines for initial *A*-phase at 16100 and 22300 cm^{-1} are determined for Mo^{3+} at octahedral axial disordered complex with C_{3v} symmetry concisely. The thermal study were performed with Q-1500 and Paulik–Erdey derivatograph within the temperature range of 100–900°C. Phase composition was determined using atomic absorption and chemical analyses for Mo and P.

A Brucker ESR 200tt spectrometer operating at X-bands was used to record the ESR polycrystalline spectra of the *A* and *B*. IR spectra of *A* and *B* samples were measured in the range 400–1400 cm^{-1} on UR-20 spectrophotometer. By XPS method of investigation the molybdenum atoms at different valence state on catalyst surface have been indicated using Au line as internal standard. The work function of specimens were measured at catalytic stream type reactor at excess of oxygen (1.5% CO, 20% O_2, 78.5% He) with chromatographic analyses of reaction mixture components (CO, O_2, CO_2). After pretreatment with working mixture at temperature 573 K, catalytic activities of patterns have been measured.

Results and discussion

The results from the derivatographic studies of initial specimens *A* are represented in Fig. 1.

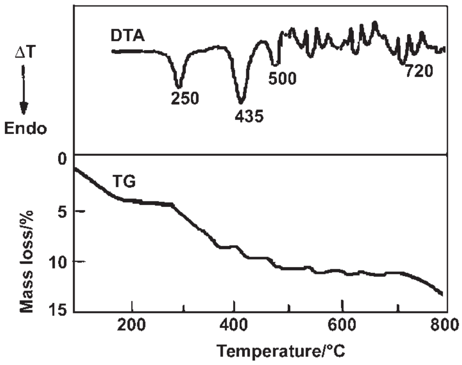

Fig. 1 DTA and TG curves of powder *A*

The DTA curve is characterized by two endothermic peaks at 200, 435°C and series of endothermic effects in the range of 550–720°C. The first endothermic effect is accompanied by a decrease in mass of the sample and it can be ascribed to the removal of the water of crystallization. The second and third endothermic effect at 435, 500°C is of special interest. It can be associated with series stage of *A* oxidation to mixed *A/B* product. This assumption is supported by the fact that a microscope observation of the sample A partial oxidation and surface disturbance. At the temperature range 500–720°C deepening of *A* surface distraction and also *B*–phase formation can be observed. The TG curve in Fig. 1 shows that at temperature 500°C the sample mass decreased. It should be noticed that small mass losses are characterized of slow process of *A* surface partial oxidation. Considering the powder X-ray investigation results we believe that a rather abrupt mass loss at 435°C is estimated to transformation:

$$1/2O_2+Mo(PO_3)_3 \Rightarrow MoOPO_4+P_2O_5 \uparrow \text{ (mass loss).}$$

The existence of two levels of interaction has been established. At the first stage from the surface of $Mo(PO_3)_3$ gaseous P_2O_5 is evaporated. But at the DTA curve no exothermic peak estimated to a crystal state $MoOPO_4$ formation was found. Scan temperature inertia at thermogravimetry cell might be dealt with. The second stage of the single $MoOPO_4$–phase formation on $Mo(PO_3)_3$ defined by above-mentioned methods of analyses. Temporal characteristics of matrix oxidation are derived that thickness of $MoOPO_4$ layers growths proportionally to time of addition (Fig. 2).

On the sample surfaces no method, neither XPS nor electron absorption spectroscopy, indicated Mo^{4+} on the pattern surface after oxidation. The IR absorption bands associated with $P_3O_9^{3-}$ anion slowly disappeared at temperature corresponding to the TG transition. The ESR spectra of obtained material consist of broadcast line with g~2 of Mo^{3+} at trigonal disordered octahedral field and sharp signal with $<g>$~1.8 of Mo^{5+} at tetragonal crystal field of symmetry. Intensity of *d-d* transition at Mo^{3+} complex and sharp signal with $<g>$~1.8 of Mo^{5+} at tetragonal crystal field vanished at 900°C.

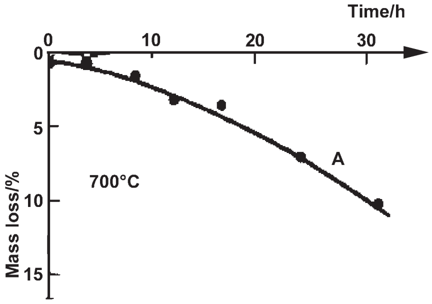

Fig. 2 Dependence of mass change of the powder *A* at 700°C

In order to determine if these materials could be used as catalyst, i.e. if it were possible to generate any catalytic active sites on surface, we examined the mixed $Mo(PO_3)_3/MoOPO_4$ patterns at CO oxidation reaction. Preliminary measurements of work function temperature dependence and specific adsorption on these specimens have been made. It is found that for $Mo(PO_3)_3/MoOPO_4$ series specimens specific adsorption value lower than for MoO_3, but equal with pure $Mo(PO_3)_3$ and $MoOPO_4$. The work function value at 300°C rises more than $10–10^2$ times compared with all abovementioned pure samples.

The results obtained by derivatographic analysis on the thermal stability of Mo–O–P catalysts were confirmed by X-ray studies and chemical analyses. It is evident that the intensity of the reflections characteristic of $MoOPO_4$ increases twice at temperatures up to 500°C due to a higher degree of crystallinity of the compound. After that the signal intensities noticeably decrease due to its evolution at high temperatures at 700–900°C. The XPS analyses show that $MoOPO_4$ remains constant up to 700°C and then begins to decrease.

The investigations on the thermal stability of the system Mo–O–P lead to some conclusions on the possibility of the preparation of active catalysts for CO oxidation, which would have a longer lifetime than initial *A* used at present [3]. As was already pointed out, the main reasons to use partial oxidation for industrial molybdenum-phosphate catalysts creation. The active component of Mo–O–P catalysts is MoO^{2+} groups, which is a stable compound showing no substantial changes under the conditions, and attribute to a lot of technological processes [3]. The thermal properties of the mixed catalysts enable to assume that the Mo–O–P catalysts proposed by us are of a definite interest in view of their future application in practice.

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