



Synthesis and Properties of Ag / CuO / SiO₂ Nanocomposites

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In this paper the composites Ag / SiO₂ with regularly distributed in bulk matrix silver and copper oxide nanoparticles were synthesized. Herewith, copper ions was introduced into porous support at the stage of sol-gel synthesis. Sample Ag / CuO / SiO₂ was tested by the catalytic reaction of CO oxidation and compared with Ag / SiO₂. It was revealed that sample with introduced copper show lower activity. This fact can be explained by formation of silver cuprate during preparation of composite Ag / CuO / SiO₂. Treatment by reaction mixture (CO and O₂) led to release of silver in ionic, clusters and metal states that increased catalytic activity of the composite.

Keywords: Silica, Monolith, Silver, Copper oxide, Nanoparticles, Low-temperature Catalytic oxidation of carbon.

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1. INTRODUCTION

Low-temperature catalytic oxidation of carbon monoxide (LTO CO) to CO₂ is one of the most perspective process for cleaning up the environment. Different composites are used as the catalysts, for example, supported precious metal catalysts which are known it's high activity in oxidation CO. Blocked porous silica prepared using sol-gel synthesis was used as a support in this work. Silver nanoparticles uniformly distributed in the pores was used as an active component. Catalytic activity of such composites depends on both oxidation state and size of active component - silver and properties of matrix surface, which controlled by structure and number of defects in it [1]. Surface defects include groups, where lattice atoms of silicon or oxygen are situated in unusual coordination or bounded to impurity atoms.

2. SAMPLES PREPARATION

The purpose of this work was to obtain the composites based on silver and silica with copper ions introduced on the stage of sol-gel synthesis and comparison of its catalytic properties with composites without copper. Thereto it was worked out the novel method based on sol-gel synthesis for production support doped by metal ions. According to this method into aqueous solution of polyethylene glycol 35 000 with catalyst for hydrolysis – nitric acid sequentially was added copper(II) nitrate and tetraethoxysilane. Further as in method for preparation of porous silica gels initial mixture was stirred at room temperature for an hour. The resulting sol was placed in sealed containers and kept for 7 days at 50 °C. The samples were then taken out of the gel containers, rinsed with deionized water and immersed in a 25 % ammonia solution for 7 days. After that samples were dried at room temperature and then subjected to heat treatment at 500 °C. Thus it was obtained sample with content of copper 5.6 % wt., morphology of

which is shown at Fig. 1. Pore size was 30-50 nm. Silver nanoparticles were obtained by filling of CuO/SiO₂ pore system with solution of silver ions and formamide with following reduction. The content of silver was 3 % wt, particle size was ~ 10 nm. Samples Ag/SiO₂ was prepared by the same method without introduction of copper (II) nitrate on the stage of synthesis of silica support.

3. SAMPLES PROPERTIES

The catalytic properties of samples Ag/SiO₂ and Ag/CuO/SiO₂ in CO oxidation were examined in an automated system with flow reactor and mass-spectrometric analysis of gas mixture. Previously, we revealed that composites Ag/SiO₂ obtained by described above method gained low-temperature activity ($T < 100$ °C) after oxygen-reduction (OxRed) treatment [1]. Fig. 2a shows dependence of CO conversion on temperature for samples Ag/SiO₂ before OxRed treatment and after it. In accordance with Fig. 2a catalytic activity revealed at room temperature, it means appearance of LTO CO (marked off by circle).

As a consequence of similar OxRed treatment of composite Ag/CuO/SiO₂ it was turned out, that this composite in spite of essential activation and shift of temperature profile of activity on ~100 °C didn't display low-temperature activity at the CO oxidation reaction (Fig. 2b). However, after sample was treated by the reaction mixture reasonable low-temperature activity of copper contained composite was observed at the next cycle (Fig. 3).

According to the presented data, samples respond to treatment by reaction medium or oxygen and hydrogen in different ways. It was made a conclusion, that copper containing samples were activated by reaction medium. Forming silver cuprates Ag_xCu_yO_z [2, 3] during synthesis or OxRed treatment can explain such behaviour of composites. This cuprates don't let silver participate in

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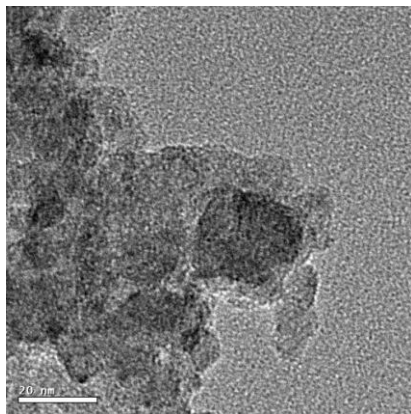


Fig. 1 – TEM-image of sample CuO/SiO₂

catalytic reaction in contrast to samples without copper where silver distributes on the surface of support in metal, cluster and ion states forming active sites for catalytic reaction.

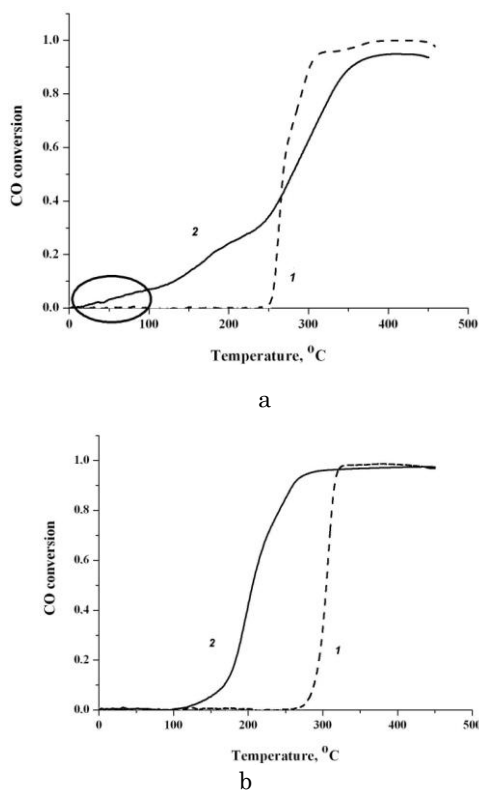


Fig. 2 – Dependence of OxRed treatment on catalytic activity of composites Ag / SiO₂ (a) and Ag / CuO / SiO₂ (b). Before (1) and after (2) treatment

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Spectra of diffusion reflection in UV-vision region for samples Ag / CuO / SiO₂ before and after participation in catalytic reaction of CO oxidation were analyzed for identification of silver forms in copper containing composites. Reflection spectra were converted by Kubelka-Munk transformation. It was turned out that after treatment by reaction mixture in simple Ag/CuO/SiO₂ silver released in ion forms proved by appearance of peak at 245 nm, clusters – peak at 324 nm and nanoparticles – maximum at 397 nm (Fig. 4).

4. CONCLUSIONS

Thus, there were all silver species which were necessary for LTO CO after treatment of composites Ag/CuO/SiO₂ by reaction mixture. This effect of reaction mixture could be connected with formation and decomposition of carbonates and formates of copper and releasing of active silver in the forms of particles, clusters and ions.

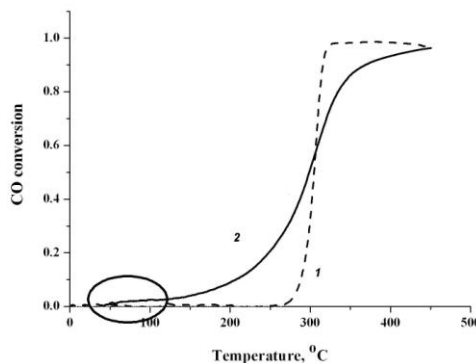


Fig. 3 – Dependence of reaction medium on catalytic activity of samples Ag / Cu / SiO₂. Before (1) and after (2) treatment

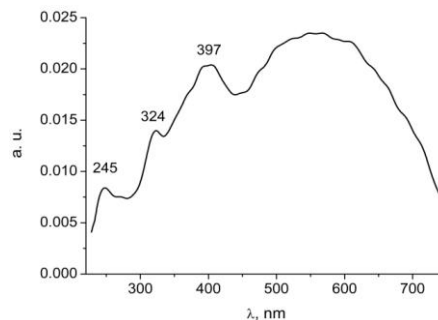


Fig. 4 – Remainder between adsorption spectra of samples Ag / Cu/SiO₂ after OxRed treatment and exposure of reaction mixture and after only OxRed treatment