

# INFLUENCE OF THE PHOSPHATE ADDITION ON THE ACTIVITY OF AG- AND CU-SUPPORTED CATALYSTS FOR SELECTIVE OXIDATION OF ETHYLENE GLYCOL

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## Introduction

Polycrystalline Cu and Ag catalysts are used extensively for partial oxidation of alcohols (methanol, ethanol, ethylene glycol, etc.) into carbonyl compounds. However, activity of polycrystalline catalysts decreases as a result of catalyst surface sintering as well as carbon deposits formation under the action of “hard” catalytic process conditions [1]. New catalysts representing Ag or Cu nanoparticles supported on silica- or zirconia-phosphate systems are free from such disadvantages, and the presence of phosphate component provides increase in selectivity in the course of ethylene glycol oxidation into glyoxal.

## Experimental

Silver and copper nanoparticles supported on silica, silica-phosphate and zirconia-phosphate were prepared by impregnation and sol-gel methods, and investigated using a complex of physical-chemical methods such as UV-VIS, FTIR, SEM, TEM HR, XRD and XPS. The TPO, H<sub>2</sub> TPR and CO TPR methods were used to estimate the catalyst surface reactivity. CO TPR was used for detection of deep oxidation surface species. Active component states as well as dynamics of reversible oxidation-reduction of active component during the cyclic treatment in TPO/TPR conditions over model systems were studied.

## Results/Discussion

It was shown that Ag and Cu nanoparticles (5-50 nm) are formed on the silica surface. It was shown that certain thermal oxidative conditions allowed forming small Ag particles on the silica surface. Strong interaction of small silver particles (less than 10 nm) with silica is explained by electron depletion (UV-VIS, XPS) and amorphous structure (XRD, TEM HR) of silver particles that leads to increase in activity towards CO.

The introduction of phosphate on the surface of silver supported on silica led to redistribution of silver. The formation of silver ions and/or clusters stabilized by phosphate was observed after the thermal oxidative treatments. In case of Cu-containing systems copper oxides

stabilized by phosphate and the copper phosphate formation occurred during the oxidative treatments. The increase in phosphate content led to growth of a part of copper phosphate, while copper oxides formation process remained steady.

The reversible oxidation/reduction of active components was observed during TPO/H<sub>2</sub> TPR experiments. During the TPR experiments after oxidative pretreatment in TPO conditions the reduction of Ag ions occurred up to 40-50% from the total Ag loading [2]. Increase in the phosphate modifier amount did not result in enhancement of Ag amount reduced during the H<sub>2</sub> TPR. This indicated the establishment of equilibrium between reduced and oxidized states of silver. The amount of Cu, reduced in TPR conditions, decreased after several cycles of TPO/TPR treatments. This was associated with crystallization of copper oxides and copper silicate (XRD, XPS, TEM HR).

According to CO TPR data the room temperature activity in CO oxidation reaction was observed for Ag/SiO<sub>2</sub> catalyst after certain TPO pretreatment. CO oxidation by Cu/SiO<sub>2</sub> was observed above 230 °C. Ag/SiO<sub>2</sub> with phosphate addition did not have reactivity towards CO oxidation. The phosphate addition on the surface of Cu/SiO<sub>2</sub> led to decreasing of the amount of oxidized CO, and reaction began at 270 °C.

The investigation of Zr-containing systems was complicated by spillover of atomic oxygen from variable valent Zr to silver particle surface. It led to the increasing of oxidative ability towards CO oxidation. The mobility of atomic oxygen in zirconia-phosphate system was less than the one in zirconia, and spillover of oxygen was complicated. The excess of amorphous phosphate prevented the reaction of CO with the catalyst surface.

Thus, addition of phosphate on the surface of catalytic oxidative systems may be used to govern the reactivity. Phosphate blocks the total oxidation sites increasing the selectivity with respect to partial oxidation of alcohol.

It was shown that reversible oxidation-reduction of the active component took place in Ag- and Cu-containing catalytic systems. The addition of phosphate modifier led to increase in the active component mobility and localization of active component in subsurface layer of the catalyst. This increased the catalytic activity of such systems in the processes of partial oxidation of alcohols. This approach allowed forming the active catalyst surface under the action of reaction conditions. This also resulted in solution of surface sintering and carbon accumulation problems, which are typical for polycrystalline Cu and Ag catalysts.

## Acknowledgement

This work was supported by the Russian Federal Program “Scientific and scientific-educational professional community of innovated Russia”.

## References

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