

Selective oxidation of alcohols over Ag-containing Si₃N₄ catalysts

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Introduction

It is known that Ag-based catalysts are widely used in industry for production of aldehydes such as formaldehyde, glyoxal, etc., in the alcohol-rich adiabatic mode. The nature and properties of catalyst support are very important for creation of highly selective catalytic systems. Ceramic materials based on silicon nitride provide such advantageous properties as high thermal conductivity, high hardness and strength, and therefore, can be considered as promising materials for application as a silver catalyst supports to be used in selective oxidation of alcohols into carbonyl compounds. A comparison of activity/selectivity of Ag-containing materials in high temperature alcohol-rich oxidative process and low-temperature oxygen-rich process as well as their dependence on the phase composition of silicon nitride-based supports is of particular interest. The aim of the present work was to perform a comparative investigation of Ag-containing catalysts supported on silicon nitride during the selective oxidation of ethylene glycol and ethanol into corresponding aldehydes.

Experimental

In the present work Ag-containing silicon nitride catalysts (Ag loading was ~ 5 % mass.) were prepared by deposition of CF₃COOAg layers on the support surface from toluene with subsequent decomposition in air at 550 °C as described earlier in [1]. In the present work three types of silicon nitride samples, namely, Si₃N₄, Si₃N₄-Zr and Si₃N₄-Al, prepared by self-propagating high-temperature synthesis (SPS) using FeS₂ nitriding were used as silver catalyst supports [1]. Before addition of silver the support grains were treated by hydrochloric acid for removal of Fe admixture.

The catalytic investigations were performed in a flow tubular quartz reactor with a stationary layer of catalyst at 500 and 620 °C (for ethylene glycol oxidation) and in temperature range of 150-450 °C for ethanol oxidation. The test conditions for ethylene glycol oxidation in alcohol-rich reaction mixture and ethanol oxidation in oxygen-rich reaction mixture were presented in [1, 2]. The catalysts prepared were characterized using X-ray diffraction, scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyses (EDX) unit, and transmission electron microscopy (TEM). Chemical composition of catalyst samples prepared was controlled by ICP-AES method.

According to XRD results obtained the phase composition of the prepared supports was Si₃N₄ (β-Si₃N₄ – 85 %, α - Si₃N₄ – 15 %); Si₃N₄-Zr (α - Si₃N₄ – 12 %, β - Si₃N₄ – 60 %, ZrO₂ – 28 %) and Si₃N₄-Al (α-Si₃N₄ – 9,5 %, β-Si₃N₄ – 81 %, Si₃Al₁₂O₉N₁₀ – 9,5 %.).

Results/Discussion

Preparation of Ag-containing ceramic material from organic media allowed obtaining the catalyst with highly stabilized Ag particles with homogeneous distribution [1]. It was shown that glyoxal selectivity was 41 % while ethylene glycol conversion was 76 % for Ag/Si₃N₄ catalyst prepared from organic media. An influence of chemical and phase composition of Si₃N₄-based ceramics supports was investigated. It was shown that the presence of ZrO₂ and Si₃Al₁₂O₉N₁₀ phases in the support composition allowed increasing the glyoxal selectivity up to 54 % at 97 % glycol conversion. However, the presence of Fe-containing additives on the support surface led to decrease in glyoxal selectivity. The formation of products as a result of oxidation of one functional group of ethylene glycol molecule (i.e., glycolic aldehyde, glyoxalic and glycolic acids) was observed during the high temperature ethylene glycol oxidation.

Ag-containing ceramic catalysts were characterized by high selectivity/activity in the course of ethanol oxidation into acetaldehyde at 300 °C. For all the catalysts investigated the selectivity reached values up to 95 % at 100 % conversion. It was shown that the support phase composition did not influence the selectivity/activity of catalysts during the ethanol oxidation in oxygen-rich reaction mixture. To achieve high selectivity with respect to desired aldehyde in the course of low temperature oxygen-rich conditions it was necessary to provide additional activation of Ag-containing sites. In the present work we proposed the participation of Fe-containing additives in the process of activation of selective sites forming on the Ag surface during oxygen adsorption. It is noteworthy that the high values of selectivity and alcohol conversion mentioned were observed in oxygen-rich reaction mixture, where oxygen content was 18 % vol., ethanol content was 2 % vol.

Thus, the main reason for achievement of high activity/selectivity of Ag-containing catalysts during the selective alcohol oxidation is one-way action of addition agent and active component. In case of diol oxidation the monodentate ethylene glycol adsorption on Fe-containing sites led to decrease in selectivity with respect to glyoxal. This situation was not observed during the ethanol oxidation into acetaldehyde.

References.

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