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ABSTRACTS

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Silica-Supported Silver-Containing OMS-2 Catalysts for Ethanol Oxidative Dehydrogenation

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1 Introduction

High activity of supported silver catalysts in selective oxidation of alcohols was shown in many studies [1, 2]. Catalytic activity of Ag-containing catalysts, in particular, Ag/SiO₂, may be increased by addition of transition metal oxides [3]. Manganese oxides are expected to be suitable modifiers for Ag/SiO₂ catalyst due to reversible Mn⁴⁺/Mn³⁺ redox cycle. It is known that silver-containing cryptomelane-type manganese dioxide catalysts (Ag/OMS-2) have high activity and selectivity in oxidation of alcohols, in particular, octanol-1 and ethanol [4, 5]. However, oxidation of ethanol over OMS-2 catalysts is carried out using gas mixture containing low concentration of oxygen, generally 1-10 vol. % [5, 6] because of high activity of these catalysts in deep oxidation. One of the ways to control the redox, catalytic and acid-base properties of metal oxides is the use of different supports. The purpose of present research work is to design the method to prepare highly effective Ag/OMS-2/SiO₂ catalysts and investigate their catalytic properties in oxidative dehydrogenation of ethanol.

2 Experimental

To prepare Ag/OMS-2 catalysts two different methods were used. At first, OMS-2 sample was prepared by procedure described in [7], and then it was impregnated with water solution of AgNO₃ followed by calcination in air flow at 500 °C (Ag/OMS-2-I). In the co-precipitation method (CP) AgNO₃ was added in course of preparation of OMS-2. Nominal amount of Ag was 5 % wt. The Ag/OMS-2/SiO₂ catalysts were prepared by the sequential impregnation (SI) and co-precipitation (CP) methods. In the first method silica was impregnated with appropriate quantity of KMnO₄ solution and then dried at 60 °C. The obtained KMnO₄/SiO₂ sample was added into the acidified water solution of Mn(NO₃)₂ under stirring. After that the obtained mixture was heated in autoclave for 24 h, then the precipitate was filtered, washed and dried. The obtained OMS-2/SiO₂ sample was impregnated with water solution of AgNO₃ followed by calcination in air flow at 500 °C. According to the second method, KMnO₄/SiO₂ was added into the mixed solution of Mn(NO₃)₂ and AgNO₃. The catalysts were characterized by TPR-H₂, TPO, TPSR-C₂H₅OH, XRD, TEM, AES and N₂ adsorption at -196 °C. Catalytic activity of the samples in ethanol oxidation was tested in a flow fixed-bed reactor at atmospheric pressure using 0.5 g of catalyst. Gas mixture containing 2 %vol. C₂H₅OH and 18 vol. % O₂ in He was passed through reactor at total flow rate of 60 cm³/min. The effluents from the reactor were analyzed by on-line gas chromatography. Prior to catalytic experiment the catalysts were treated in 8 % O₂/He at 500 °C for 1 h.

3 Results and discussion

Investigation of chemical composition of the prepared catalysts revealed that using of co-precipitation method (CP) resulted in partial loss of Ag due to leaching of silver in course of hydrothermal treatment.

The OMS-2, Ag/OMS-2-I and Ag/OMS-2-CP catalysts were used as model systems for detailed characterization of supported catalysts. To investigate the effect of silver addition on the active sites of OMS-2 TPSR of adsorbed ethyl alcohol were carried out. Formation of water was observed for all catalysts at 80 °C in course of ethanol adsorption in pulse mode, therefore adsorption and dehydration of ethanol occurred on the acid sites. The quantity of adsorbed alcohol was 221, 172 and 142 $\mu\text{mol/g}$ for OMS-2, Ag/OMS-2-CP and Ag/OMS-2-I catalysts, respectively. Carbon dioxide was the main product of TPSR and released at 170 and 230 °C. Investigation of catalytic activity of prepared OMS-2/SiO₂, Ag/OMS-2/SiO₂-SI and Ag/OMS-2/SiO₂-CP catalysts in oxidative dehydrogenation revealed that addition of silver results in increasing of the ethanol conversion. This may be explained by increasing of reaction ability of surface oxygen in the presence of silver, which was confirmed by TPR-H₂. The effect of silver content and Mn/Ag molar ratio on the catalytic properties was investigated. It was stated that silver content insignificantly effect on the ethanol conversion. However, selectivity towards acetaldehyde depends on silver content. For Ag/OMS-2/SiO₂-CP catalyst the selectivity towards acetaldehyde at temperatures above 200 °C is lower in comparison with the one for Ag/OMS-2/SiO₂-SI due to low silver content (higher molar ratio Mn/Ag) or formation of mixed Ag-Mn phase in course of synthesis via co-precipitation.

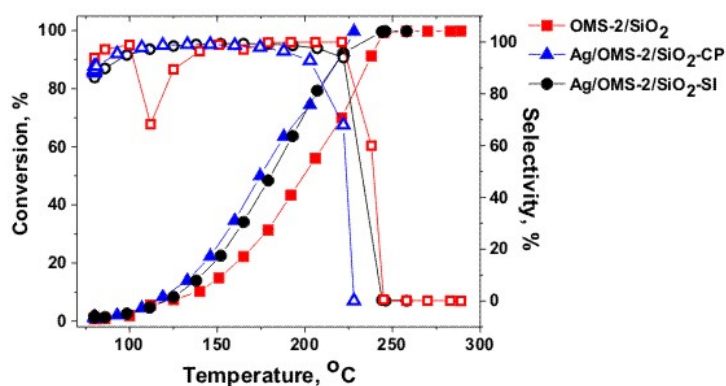


Fig. 1. Catalytic properties of OMS-2/SiO₂, Ag/OMS-2/SiO₂-SI and Ag/OMS-2/SiO₂-CP

Generally, deep oxidation activity of Ag-containing supported catalysts is higher than the one for OMS-2/SiO₂, which may be associated with increasing of reoxidation ability in presence of silver (according to TPO data).

4 Conclusions

The Ag/OMS-2/SiO₂ and OMS-2/SiO₂ catalysts were synthesized and tested in ethanol oxidation. It was stated that silver addition increases the reducibility and reoxidation ability of OMS-2, as a consequence catalytic activity increases. Catalytic properties of Ag/OMS-2/SiO₂ catalysts may be controlled by variation of Mn/Ag molar ratio and preparation method.

Acknowledgements

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