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The role of metal–support interaction in Ag/CeO₂ catalysts for deep and selective oxidation of organic compounds

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The metal–support interaction plays an important role in the designing of the catalysts with both enhanced activity and stability. It is known that CeO₂ and TiO₂ are more favorable supports for catalysts with the strong metal–support interaction (SMSI) due to chemical features and semiconducting properties [1]. The SMSI is connected with both changes of the structures of metal and support at the interface and a redistribution of the electronic density between metal and support (electronic metal–support interaction). These phenomena lead to the formation of defects, oxygen vacancies, local charges near the metal–interface boundary that provide an increased catalytic activity. The key challenge is to elaborate the synthesis approaches to designing the catalysts with enhanced metal–support interaction.

The present work is devoted to the designing of the Ag/CeO₂ and Ag-CeO₂/SiO₂ catalysts with controllable Ag–CeO₂ interfacial interaction. The co-deposition precipitation (co-DP) and impregnation (imp) techniques were used to synthesize the Ag/CeO₂ catalysts with different metal–support interaction. To control the interaction of Ag and ceria on the silica surface, the consecutive and simultaneous impregnation of the silica by silver and ceria precursors (corresponding nitrates) were applied. Also the impregnation of the pre-reduced CeO₂ or CeO₂/SiO₂ support with an aqueous solution of AgNO₃ was used. It was found that the redox reaction between the Ag⁺ and Ce³⁺ in the solution or on the surface of the pre-reduced ceria particles led to enhanced Ag–CeO₂ interfacial interaction. The SMSI was confirmed by the XRD (increased cell parameter of CeO₂), TEM (epitaxial growth of Ag particles with the size of 2–4 nm on the surface of ceria in spite of a large difference of the corresponding interplanar distances of ~25%). The predominant distribution of the Ag particles on the surface of CeO₂ or at the CeO₂–SiO₂ interface was found by the TEM HR for the Ag-CeO₂/SiO₂ catalyst prepared by the impregnation of the pre-reduced CeO₂/SiO₂ support. It was shown by Raman spectroscopy that the enhanced Ag–CeO₂ interfacial interaction led to an increased concentration of oxygen vacancies in the CeO₂ structure. The results of the TPR-H₂ method also confirmed the increased reducibility of the CeO₂ surface in the presence of silver caused by the enhanced metal–support interaction.

All this factors, namely, an increased defectiveness of ceria particles, the formation of oxygen vacancies and a high reducibility of ceria, lead to the growth of the catalytic activity in oxidation reactions. Thus, an increased catalytic activity of the Ag/CeO₂ catalysts with SMSI was found for low-temperature CO oxidation, soot combustion and oxidative dehydrogenation of ethanol into acetaldehyde [2]. It was shown that the distribution of Ag and CeO₂ on the surface of silica support influenced on the activity in ethanol dehydrogenation. The enhanced Ag–CeO₂ interfacial interaction in Ag-CeO₂/SiO₂ catalyst, prepared by impregnation of the pre-reduced CeO₂/SiO₂ support [3], was found, and an increased activity in oxidation was observed with maintaining of the high selectivity toward acetaldehyde.

Thus, the metal–support interaction plays an important role for CeO₂-containing catalysts in oxidation of organic compounds. The co-deposition, simultaneous impregnation and impregnation of the pre-reduced ceria may be used to design the catalysts with an enhanced metal–support interaction. The redox reaction between the metal precursor and Ce³⁺ aqueous or surface species leads to the formation of the SMSI.

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References

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