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Design of Ag-CeO_2 catalysts with strong metal-support interaction for selective reduction of nitroarenes into corresponding amines

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The selective reduction of nitroarenes to corresponding amines is of great importance, because amines are an important precursor for the synthesis of dyes, pesticides and pharmacological preparations in chemical industry [1]. The development of more active, selective and eco-friendly catalysts, as well as ways to carry out amine synthesis in mild conditions, is important for both basic researches and for industrial applications. The aim of this work was to synthesize and study CeO_2-based catalysts for the selective reduction of nitro compounds.

Series of Ag-CeO_2 catalysts with molar ration Ag:Ce=2:8 were prepared by two techniques: co-precipitation of $Ce(NO_3)_3$ and $AgNO_3$ by aqueous ammonia solution [2] (samples Ag-CeO_2-1 and Ag-CeO_2-2) and incipient wetness impregnation of ceria by aqueous solution of $AgNO_3$ [3] (sample Ag/CeO_2). Then, samples were dried at 120 °C of 2,5 h and calcined in air flow at 500 °C of 4 h. Catalysts were characterized by low-temperature N_2 adsorption, TPR, UV-vis spectroscopy and tested in reaction of reduction of nitrophenol by $NaBH_4$ in aqueous solution at room temperature and atmospheric pressure.

According to low-temperature N_2 adsorption data, isotherms of N_2 adsorption-desorption for all samples are characterized by the hysteresis loop, which indicates on the mesoporous structure of catalysts. CeO_2 is characterized by a specific surface area of 28 m^2/g and pores of 2-30 nm. The Ag/CeO_2 specific surface has 11 m^2/g and pores of 5-30 nm, which indicates the distribution of silver mainly in shallow pores of the support. A significant decrease in the specific surface area for catalysts is due to the high silver content of 20 % mol. The sample of Ag-CeO_2_2 has a specific surface area of only 5 m^2/g, which may be due to the most complete oxidation-reduction reaction between Ag^+ and Ce^{3+} ions in the solution during the deposition stage in an alkaline medium.

The features of reduction of catalysts were studied by the method of temperature-programmed reduction by hydrogen (TPR H_2). The reduction of CeO_2 is characterized by the presence of two temperature regions: peak at 700-900 °C is associated with the reduction of the volume of CeO_2 particles, while peak at 220-600°C may be attributed with the reduction of the surface of the CeO_2 particles. For Ag-containing catalysts low temperature H_2 consumption at 100-150°C mainly may be associated with reduction of AgO_x species. However, disappearance of peak at 300-600 °C of reduction of surface CeO_2 indicates on simultaneous reduction of AgO_x species and surface CeO_2 at 150-200 °C. Increased intensity of this peak for catalysts, prepared by co-precipitation indicates on the strong interaction between active component and CeO_2 particles.

The catalytic properties of the catalysts were studied in the reduction reaction of n-nitrophenol with sodium borohydride ($NaBH_4$) at room temperature and atmospheric pressure. CeO_2 does not catalyze the reduction of 4-nitrophenol. The introduction of silver into the catalyst promotes the reaction. Thus, on the Ag/CeO_2 catalyst, the reduction of p-nitrophenol proceeds in 15 minutes, and ones over the catalysts prepared by the co-precipitation method was 9-12 min. Thus, Ag-CeO_2_1 and Ag-CeO_2_2 are more active in this reaction that we attribute with stronger metal-support interaction in these catalysts.

Thus, it was shown that the method of catalyst preparation (impregnation and precipitation) affects the structures of the formed Ag-CeO_2 catalysts and metal-support interaction. This interaction affects the oxidation-reduction properties of the catalyst and catalytic activity in the selective reduction of nitrophenol in mild conditions.

References

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