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Formation of surface electronic states of silver and gold on different oxide supports

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Abstract

Silver and gold have unique catalytic properties in some processes, such as methanol selective oxidation, ethylene epoxidation, etc. Fundamental understanding of the coordination structure and electronic state of the active species is important in the design and development of applicable catalysts having high activity and selectivity. Comparative features in formation of different electronic states of silver and gold on oxide supports and in zeolites have been studied by the methods of IR-spectroscopy, UV-visible spectroscopy, XRD, TEM.

Spectroscopic studies of Me/ γ -Al₂O₃ after redox treatments with O₂ and H₂ identified different electronic states of silver and gold on the support surface: isolated ions, Me⁺ ions in the charged clusters, partly charged Me ^{δ^+} states in Me_n clusters, Me⁰ states in Me_n clusters.

Modifying additives of rare and rare-earth metal oxides change notoriously the electronic state of supported metals that results in the shifts of the position and intensities of absorption bands in IR and UV-vis spectra. These effects are caused not only by differences in the metal particle dispersivity, but by interaction of Ag and Au atoms and ions with Lewis acid sites of the modified support. Doping the support by Ce, La and Zr oxides results in formation of a large number of the metal stabilization sites (Zr⁴⁺, Ce⁴⁺, Ce³⁺, La³⁺) on support surface. This increases dispersivity of the metal and also slows down surface diffusion of atoms and ions when heating (XRD and HRTEM data). Additions of Ce and Zr oxides exert an electron-seeking effect on supported silver and gold, stabilize the oxidized state of the metals and increase the effective charge of the metal ions. In contrast, La and Cs oxides lower the effective charge of Me⁺ and Me ^{δ^+} and favor their fast reduction during redox treatments. The Me⁺ ions located on the surface of metal particles, experience considerably smaller influence of the modifier than the ones located on support surface, mainly by changes of the collective electronic properties of the clusters.

According to UV-Visible and XPS data three different types of gold species were observed in zeolite samples. Gold Au⁺ and Au³⁺ ionic species, gold clusters those could be fitted to the intracrystalline channels of zeolites with size about molecular size in diameter and well-dispersed gold nanoparticles on the external surface of zeolites. It was found that the variety of gold species depends on type and SiO₂/Al₂O₃ molar ratio of zeolites and its geometry, concentration of the precursor solution and the conditions of redox treatment. The samples with different gold concentration were studied for mordenites and for beta-zeolite. The relative intensity of the UV-Visible spectra absorbance increased with increasing of gold concentration for all gold species, but the contribution of different species did not change.

The influence of MR on the gold state was studied for Au-mordenites. The optical spectra showed that the contribution of the exchanged gold ions and gold clusters grows with increase of the concentration of the Brønsted acid sites, which depends on MR. It was found that the contribution of Au nanoparticles increases with the reduction temperature. Results of XRD, HRTEM and optical data showed that the size of Au nanoparticles particles is 1-3 nm for reduction temperatures < 100°C and 1-50 nm for reduction temperature $\geq 100^\circ\text{C}$.

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