Physico-chemical nanomaterials science

Understanding the behavior of catalytic systems prepared by noble metal anchoring on the silica surface

O.Yu. Boldyrieva, A.V. Yatsymyrskiy, V.V. Lisnyak

Chemical Department, National Taras Shevchenko University of Kyiv, Volodymyrska 62a, 01060 Kyiv, Ukraine. E-mail:ob@univ.kiev.ua

A series of catalytic systems were prepared by noble metal anchoring on a silica surface. The silicas employed in this work were grafted with organic groups that are used as ligands for the metal complexing. The grafted silicas were characterized with FTIR/ATR/DRIFT and thermal analysis. The anchoring passes for the expense of grafted groups and the silicas grafted with organic amine residues show excellent adsorption capacity for Pt, Pd and Au metal ions.

The reduction/oxidation of surface complexes of anchored noble metals can cause the formation of nanoparticles (np), which are a subject of this study. This particles form catalytic systems that have reasonable oxidation activity against small reductant molecules, as dihydrogen. The activity of systems was analyzed in a line with SEM and XPS data. The effect of nanoscaled particles and their surface oxidation are comprehensively considered. We propose the following traditional red-ox scheme of the oxidative catalysis at considering the reaction of hydrogen oxidation with oxygen. However, we found the phenomena when summarized the data of key literature sources with that obtained from our previous experiments. The phenomena are beyond of consideration, in the framework of usual mechanistic views on the surface interface catalysis, and have relations with nature of np surface and the catalytic reaction regimes. The interplay between metal surface complex and completely reduced surface metal of nm scaled particles is disclosed. The effects of supported metals *np* surface oxidation and reduction, the nature/action of oxidant/reductant reagents and the impact of the reaction conditions are subjected to a deep analysis. Surprisingly, obtained kinetic data cannot adequately described within the usual supposed exponential growth of reaction rate with the size of *np*. Despite that, the imaginary activation energy is low enough to be accepted as the size effect affected. The gold *np*, obtained as a reference, are efficient oxidants of H₂. They work well and could be characterized with the rate values close to other noble metals. This observation is interesting if consider the surface layer of np, in the oxidation reaction catalyzed by gas-solid interface, as a dynamically oscillated system. The nature of oscillations and bifurcation points in the hydrogen oxidation are also suggested.