Praca doktorska
Mgr Kalina Grzelak

Badanie wpływu ceru na właściwości powierzchniowe i aktywność katalityczną modyfikowanych wybranymi metalami (Ca, Nb, Pd, Cu, Ru) mezoporowatych pianek krzemionkowych

Influence of cerium on surface properties and catalytic activity on metal-modified (Ca, Nb, Pd, Cu, Ru) mesoporous silica foams

Streszczenie w języku angielskim:

Many common industrial processes are based on the use of homogeneous catalysts. Whenever possible, the replacement of the homogeneous catalysts with heterogeneous ones (e.g. solid materials) opens up the possibility of the catalyst reuse and carrying out the reaction under mild conditions. Depending on the reaction mechanism, the catalysts must have basic, acidic or redox sites on the surface. Very often the relevant chemical transformation is a multistep process which requires a mixture of different active sites. Therefore, the composition of heterogeneous catalyst plays a crucial role in its catalytic performance.

The aim of the research presented in this dissertation was to design multi-component cerium-modified heterogeneous catalysts based on mesocellular foams, active in the catalytic production of valuable chemicals. Besides cerium, the following active components of the catalysts were studied: niobium, calcium, palladium, copper and ruthenium. The investigated processes were: transesterification of ethyl butyrate with methanol, reductive condensation of acetone and hydrogenation of levulinic acid.

Mesostructured silica, i.e. mesocellular foams (MCF) were modified with metals and four series of catalysts with different additional components were prepared: i) Ca and Nb and Ce at different ratios (paper I), ii) Ce and Pd or Ca and Nb and Pd (paper II), iii) Ce and Cu or Ca and Nb and Cu (paper III), iv) various amounts of Ce and Ru (paper IV). The supports were modified with metals via impregnation method.

Porous structure of MCF was documented with the use of scanning electron microscopy and low temperature nitrogen adsorption/desorption. XPS and XRD were used to analyze the oxidation state of metals. Acidic-basic properties were measured by CO_2-TPD, FTIR spectroscopy combined with pyridine adsorption as probe molecule and test reactions. H_2-TPR measurements provided the information on the interaction between metals. Finally, the catalytic activities of the materials obtained were tested and the results were correlated with those coming from physicochemical characterization. The promoting effect of cerium has been well documented for each series of catalysts.

In paper I, MCF was impregnated with Ca present mainly in the form of CaO. Addition of small quantities of Ce and Nb was found to affect the catalytic activity in transesterification of ethyl butyrate with methanol and amongst various weight ratios of these metals (1:3, 2:2, 3:1) the non-equivalent loadings favored the production of methyl butyrate. The formation of mixed phase between Nb and Ce as a result of the metals interaction was postulated to be the reason for lower activity.

Paper II gave an insight into the impact of cerium on the catalytic activity of palladium containing catalysts in reductive condensation of acetone. Ce-modified MCF was compared with Ca-Nb-MCF and two other reference materials described in literature reports. It was documented that Ce-MCF was the most stable support for Pd nanoparticles. Ceria promoted reduction of Pd and was recognized as an effective source of basicity necessary for the condensation step.

The study presented in Paper III was a continuation of that reported in paper II and it focused on the effect of palladium replacement with copper. Cerium was proven to strongly interact with copper, leading to outstanding catalytic performance. The active sites for each reaction step of reductive condensation of acetone were identified: cerium oxide catalyzed the condensation step, Cu^{2+} was responsible for dehydration and finally, metallic copper provided hydrogenation sites.

The effect of cerium on ruthenium dispersion in MCF was studied in paper IV. The correlation between loading of cerium and Ru particle size was clearly presented. The higher the loading of Ce, the better the Ru dispersion. Nevertheless, the catalytic performance of the materials obtained in the low temperature hydrogenation of levulinic acid to γ-valerolactone was also strongly dependent on the textural parameters. Basing on these two parameters the optimal value of Ce loading was determined.