

New Pt,Rh-CeO_x Catalytic Systems Prepared from Intermetallic Compounds

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Nano-sized materials have great potential for the development of new catalysts. Noble metals supported on transition or rare earth oxides showed the promising results in various catalytic processes. It was established that oxide support influences on dispersed metal component changing its properties, in particular, resistance to the sulfur poisoning. This effect strongly depends on the homogeneity of the metal component distribution.

The aim of this study was to verify the effect of ceria support on the sulfur tolerance of Pt- and Rh-containing catalysts in the model reaction of toluene hydrogenation. The new approach in the preparation of mixed Pt (Rh)/cerium oxide catalysts included oxidative treatment of noble-metal/cerium intermetallic precursors. This preparation technique leads to formation of ultradispersed noble metal particles in cerium oxide.

The Pt-Ce and Rh-Ce intermetallic precursors were synthesized by arc-melting of stoichiometric mixtures of pure components on a water-cooled copper hearth under $5 \cdot 10^4$ Pa of argon. The alloys were crushed and oxidized in the airflow at 550°C. The samples were characterized using in situ XRD; SEM/EDS; TEM/EDS; TPD H₂ and XPS techniques. Catalytic activity and sulfur resistance of the samples were tested in toluene hydrogenation reaction in a tubular continuous flow quartz reactor under atmospheric pressure at 150°C and weight hourly space velocity (WHSV) of 0.7h⁻¹. Prior to the catalytic runs, the samples were activated at 450°C in a flow of H₂. Methylcyclohexane was the only reaction product. To study the sulfur tolerance of the catalysts, the mixture of H₂S (970ppm) in N₂ was added to the feed.

The XRD analysis showed that after oxidation of Pt-Ce intermetallic compound the sample consisted of metallic Pt and CeO₂ phases, while in the case of Rh-Ce sample metallic Rh, Rh₂O₃ and CeO₂ were detected. Activation at 450 °C in H₂ flow led to formation of Pt/CeO_x and Rh/CeO_x materials. The particle sizes of noble metals in these systems calculated by Scherrer equation were 13 and 18 nm, respectively. The broadening of the CeO₂ peaks in the XRD patterns indicated an average ceria particle size of 7-10 nm.

The initial intermetallic compounds were inactive in toluene hydrogenation. The oxidized Pt-Ce samples showed the catalytic activity comparable with the activity of pure platinum, while the activity of Rh-Ce system was significantly higher. The later sample demonstrated also the highest sulfur tolerance. The deactivation curves of oxidized samples consisted of two regions with different slopes indicating the existence of two types of active sites with different tolerance to H₂S. This conclusion was confirmed by TEM experiments over the oxidized Pt-Ce sample, which revealed the presence of ceria rich and Pt rich areas along with the areas, where Pt and ceria may form combined structures with very fine distribution of Pt and ceria. The SEM/EDS analysis of the sample, partially deactivated by H₂S, showed that sulfur was concentrated preferably on Pt rich areas. These results suggested that rapid catalyst deactivation was due to the poisoning of pure metallic sites, while mixed Pt-Ce or Rh-Ce sites were more stable to deactivation.

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