

**Новые катализаторы и каталитические процессы для
решения задач экологически чистой и
ресурсосберегающей энергетики**

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Ag and CeO₂ supported on graphene oxide as a catalyst for room-temperature 4-nitrophenol reduction

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Green chemistry is a research area of chemical science that addresses the challenges in material and technology design for both energy-efficient manufacturing and environment protection. The Ag-based nanocatalysts are in the focus of green chemistry approach as advantageous systems due to relatively low cost, low-temperature activity, nontoxicity, and facile preparation and modification procedures [1, 2]. The CeO₂ addition to the Ag-containing catalytic systems enhances the catalytic activity because of the metal-support interaction that results in the interfacial charge transfer and synergistic action of the metal and oxide active sites [3, 4]. Graphene is a two-dimensional carbon nanomaterial with a uniform slit-like microporous structure and high surface area (up to 1500 m²/g). Graphene and its derivatives (e.g., graphene oxide (GO), reduced graphene oxide (RGO)) are considered promising environmentally benign adsorbents and catalyst supports [5, 6]. This work aims to prepare the Ag-CeO₂/GO system and study the synergetic effect of the active components on the catalytic activity in the 4-nitrophenol (4-NP) reduction into 4-aminophenol (4-AP) under mild conditions.

Graphene oxide (GO) was prepared by the modified Hummers' method [7] from graphite powder. Silver- and/or ceria-containing catalysts (Ag/GO, CeO₂/GO, Ag-CeO₂/GO) were synthesized using the deposition-precipitation technique. The nominal loadings of silver and ceria in the catalysts were 5 and 10 wt.%, respectively. The synthesized samples were characterized by a set of physical-chemical methods: XRD, TGA-DSC, low-temperature N₂ sorption, UV-vis and Raman spectroscopies. Catalytic activity of the samples was tested in 4-NP reduction into 4-AP by sodium borohydride (NaBH₄) as a reducing agent at room temperature and atmospheric pressure in water medium.

According to the TGA results, in the oxidizing medium the synthesized GO support decomposes via two characteristic steps at 200 °C (decarboxylation) and 600 °C (combustion) indicating the graphene oxide structure. The combustion temperature region is shifted towards lower temperatures for Ag/GO, CeO₂/GO, and Ag-CeO₂/GO samples since the active components catalyze the support combustion. The XRD data also indicate the GO formation by the diffraction peak at $2\theta \approx 11^\circ$ that is attributed to (002) plane of the hexagonal GO lattice. Contrary to the pristine support, the Ag- and/or CeO₂-containing catalysts do not show this peak due to the wedging and distortion of layered GO structure by silver and ceria particles. According to XRD data, the average size of Ag and CeO₂ nanoparticles is 30.5 and 5.6 nm, respectively. No catalytic reaction occurs without the catalyst. The pristine support (GO) and the CeO₂/GO sample show rather low catalytic activity in the process, while the Ag-containing samples (Ag/GO and Ag-CeO₂/GO) are active, with the latter showing superior activity.

Therefore, the employed synthesis techniques allowed modifying the properties of silver species to obtain the Ag-CeO₂/GO catalyst that was an efficient system for catalytic processes, especially for the reduction of nitroaromatic compounds at room temperature and ambient pressure in water medium.

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