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ABSTRACTS

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Reduced Graphene Oxide Decorated with Ag and CeO_2 Nanoparticles Composite for 4-Nitrophenol Reduction

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Green chemistry is a novel 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]. The CeO_2 incorporation into Ag-containing systems provides the enhancement of the catalytic activity due to the metal-support interaction resulting in the interfacial charge transfer and synergistic action of the metal and oxide active sites [2, 3]. Graphene is a two-dimensional carbon nanomaterial with a uniform slit-like microporous structure and high surface area (up to 1500 m^2/g). Graphene and its derivatives (e.g., graphene oxide (GO), reduced graphene oxide (RGO)) are considered promising environmentally benign adsorbents and catalyst supports. Moreover, unique electroconductivity and synergy to metals and semiconductors allows utilizing this material as an active support in photocatalysis [4]. This work aims to prepare the Ag-CeO_2/RGO system and study its catalytic activity in the 4-nitrophenol (4-NP) reduction into 4-aminophenol (4-AP) at room temperature and ambient pressure.

Graphene oxide (GO) was prepared by the modified Hummers’ method [5]. Silver- and/or ceria-containing catalysts (Ag/RGO, CeO_2/RGO, Ag-CeO_2/RGO) were synthesized by the deposition-precipitation technique using $AgNO_3$ and/or $Ce(NO_3)_3{\cdot}6H_2O$ aqueous solutions. The nominal loadings of silver and CeO_2 in the catalysts were 5 and 10 wt.%, respectively. The synthesized samples were characterized by a set of physical-chemical methods: powder X-ray diffraction (XRD), thermogravimetric analysis (TGA), low-temperature N_2 adsorption-desorption, etc. Catalytic activity of the samples was tested in 4-NP reduction into 4-AP by sodium borohydride ($NaBH_4$) as a reducing agent at room temperature and atmospheric pressure in water medium.

According to the TGA results, in the oxidizing medium the synthesized support decomposes through two characteristic steps at 200 ^{o}C (decarboxylation) and 600 ^{o}C (combustion) indicating the graphene oxide structure. The combustion temperature region is shifted towards lower temperatures for Ag/RGO, CeO_2/RGO, and Ag-CeO_2/RGO samples since the active components catalyse the support combustion.

Fig. 1 illustrates the XRD results. The GO sample possesses characteristic reflection at $2\theta \approx 11^o$ attributed to the graphene/graphite oxide (002) phase. There is a small amount of graphite phase (reflections at 26 and 42^o) occurring due to incomplete graphite oxidation during the Hummers’ process. The reflection corresponding to graphite oxide (002) is absent for the synthesized catalysts, and those typical for graphite remain. This indicates the GO reduction to RGO during the catalyst preparation. Silver species in the Ag/RGO sample exist as large crystalline metal particles. Their size decreases in the Ag-CeO_2/RGO catalyst that indicates the role of ceria in Ag stabilization in a more dispersed state. Unlike silver, CeO_2 exists both in CeO_2/RGO and Ag-CeO_2/RGO as small nanoparticles. This is attributed to the much stronger interaction between ceria precursor and graphene oxide during the deposition-precipitation.

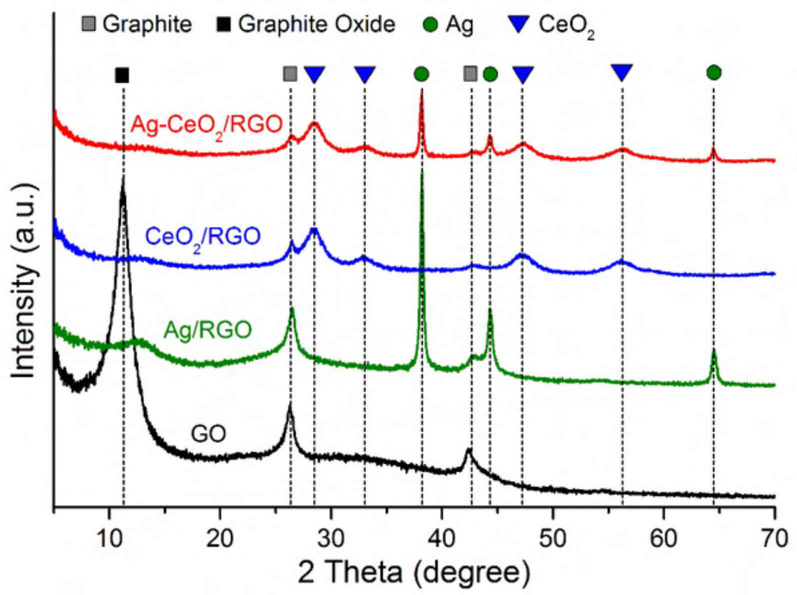

Fig. 1. XRD results for the synthesized catalysts and support

To sum up, the considered synthesis technique allows preparing the silver- and/or ceria-containing catalysts (Ag/RGO, CeO_2/RGO, Ag-CeO_2/RGO) that are advantageous and environmentally benign systems for catalytic processes such as nitroarenes reduction [6]. Joint loading of the active components results in the synergistic effect that enhances the catalytic activity. In addition, photosensitivity of Ag and CeO_2 and electroconductivity of GO support allows utilizing these systems as active photocatalysts [7].

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