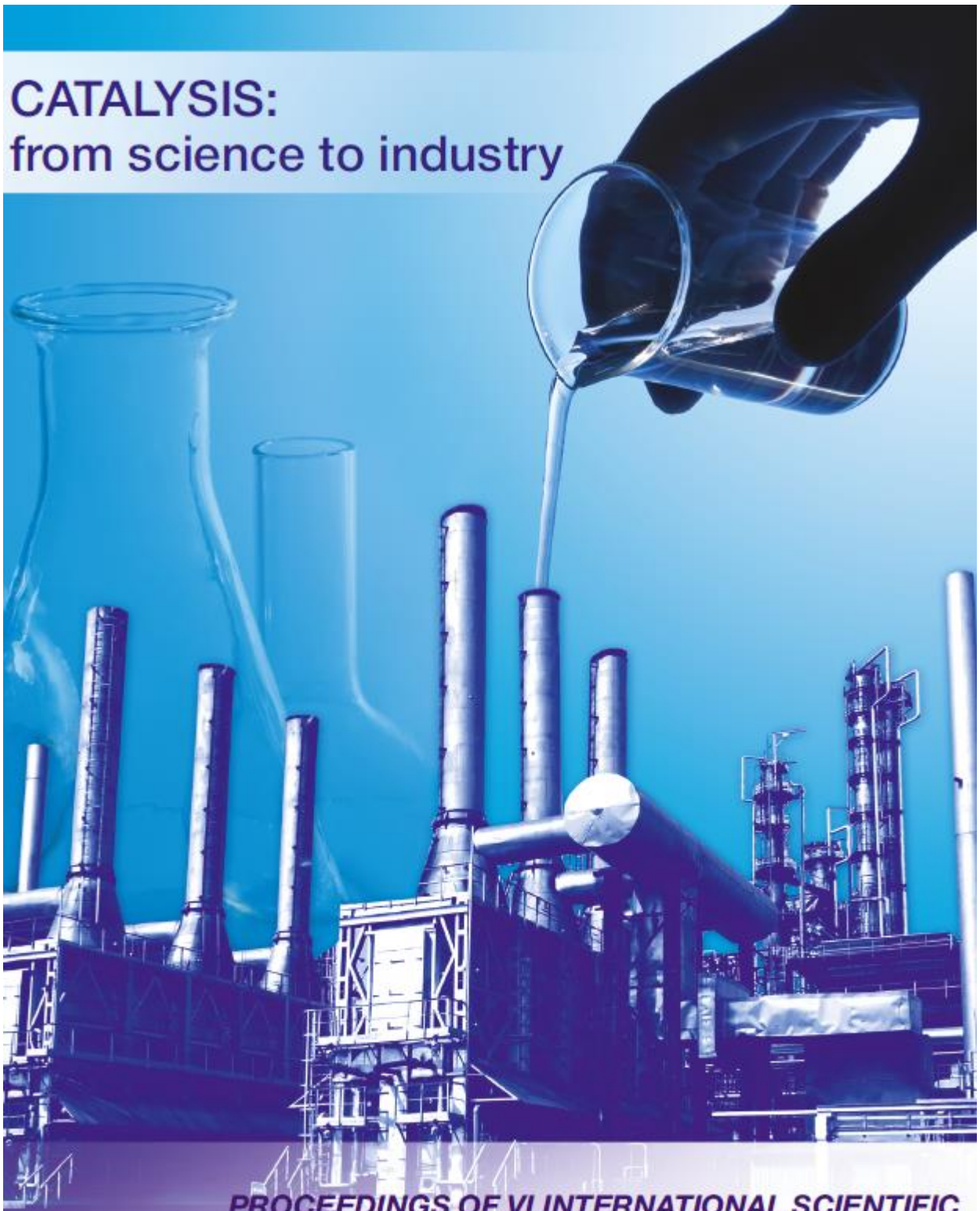
CATALYSIS:
from science to industry



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The collection is devoted to important and perspective directions of modern catalysis: fundamentals of catalyst preparation and catalytic processes, promising catalytic processes and industrial implementation of catalytic processes.

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Catalytic properties of CuO_x NPs obtained by pulsed laser ablation

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Over the past decade, copper and copper oxide nanoparticles (CuO_x NPs) have received much attention because of fundamental importance and wide potential applications in electronics, semiconductor industry, solar energy conversion, biomedicine, gas sensors, environmental science and catalysis [1]. Copper compounds are widely used as catalysts in a number of important chemical reactions such as NO_x degradation, CO oxidation, reduction of nitroaromatics, etc. [2].

The size and morphology of NPs play a significant role in developing of the chemical and physical properties and largely influence their existing applications [1, 2]. Therefore, much efforts have been dedicated to the preparation of CuOx nanostructures with different sizes and morphologies. Pulsed laser ablation (PLA) in liquid was shown to be a promising method to prepare stable dispersion of CuO_x NPs with various phase composition (Cu, Cu_2O, Cu@Cu_2O, CuO), sizes and morphology [3].

In the present work the catalytic properties of CuO_x NPs prepared by PLA of copper in different liquids were studied in reduction of aromatic nitro compounds to aromatic amino compounds in water solutions in the presence of $NaBH_4$.

CuO_x NPs dispersions (100–200 mg/l) were prepared by the PLA of copper in distilled water, ethanol, isopropanol, and aqueous solution of hydrogen peroxide (0.1 wt%) according to the technique described in Ref. [1]. The prepared samples were characterized by XRD, UV–vis absorption spectroscopy, and TEM. The catalytic properties of the CuO_x NPs obtained in reduction of p-nitrophenol (PNP) were studied using aqueous solutions of PNP and $NaBH_4$ at 19 °C. Typically, 1.7 ml of distilled water, 300 μl of the PNP aqueous solution, 300 μl of freshly prepared $NaBH_4$ aqueous solution and 200 μl of freshly prepared CuO_x NPs dispersion were used to prepare 2.5 ml of reaction mixture with the concentrations of 2.57×10^{-4} mol/l, 5×10^{-2} mol/l and 15 mg/l, respectively. The reaction was performed inside a quartz cuvette and the reduction processes were monitored online by following the optical absorption peak of PNP at 400 nm with 10 s intervals using CM 2203 spectrophotometer equipped with a magnetic stirrer and a cuvette thermostabilizer.

PLA of copper in distilled water was shown to yield cubic Cu_2O NPs, while the primary formation of the sheet-like and flower-like CuO was observed in the aqueous solution of H_2O_2. Using ethanol as the liquids for PLA of copper yields rather stable suspension of Cu NPs with a sub-monolayer of Cu_2O. All samples obtained showed catalytic activity towards selective PNP reduction to p-aminophenol (PAP), with some peculiarities depending on liquid used to prepare the CuO_x NPs dispersions. For all samples studied the induction period was observed that is usually attributed to the diffusion time required for PNP to be adsorbed onto the catalyst surface or to the time needed for $NaBH_4$ to eliminate surface oxides. The samples obtained in water and H_2O_2 aqueous solution are characterized by high catalytic activity and relatively short induction period, while the using of CuO_x NPs dispersions obtained in ethanol leads to lower activity and longer induction period. The study of the effect of alcohol adsorption and CuO_x NPs reduction by $NaBH_4$ indicated that the catalytic activity of all samples was primarily determined by the formation of Cu NPs, while the presence of alcohol in the reaction mixture affected the catalytic activity via competitive sorption with PNP on the catalyst surface.

The present research describes a facile “green” synthesis of CuOx NPs serving as catalysts for selective reduction of aromatic nitro compounds to aromatic amino compounds in aqueous solution in the presence of $NaBH_4$ that is promising for industrial application.

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