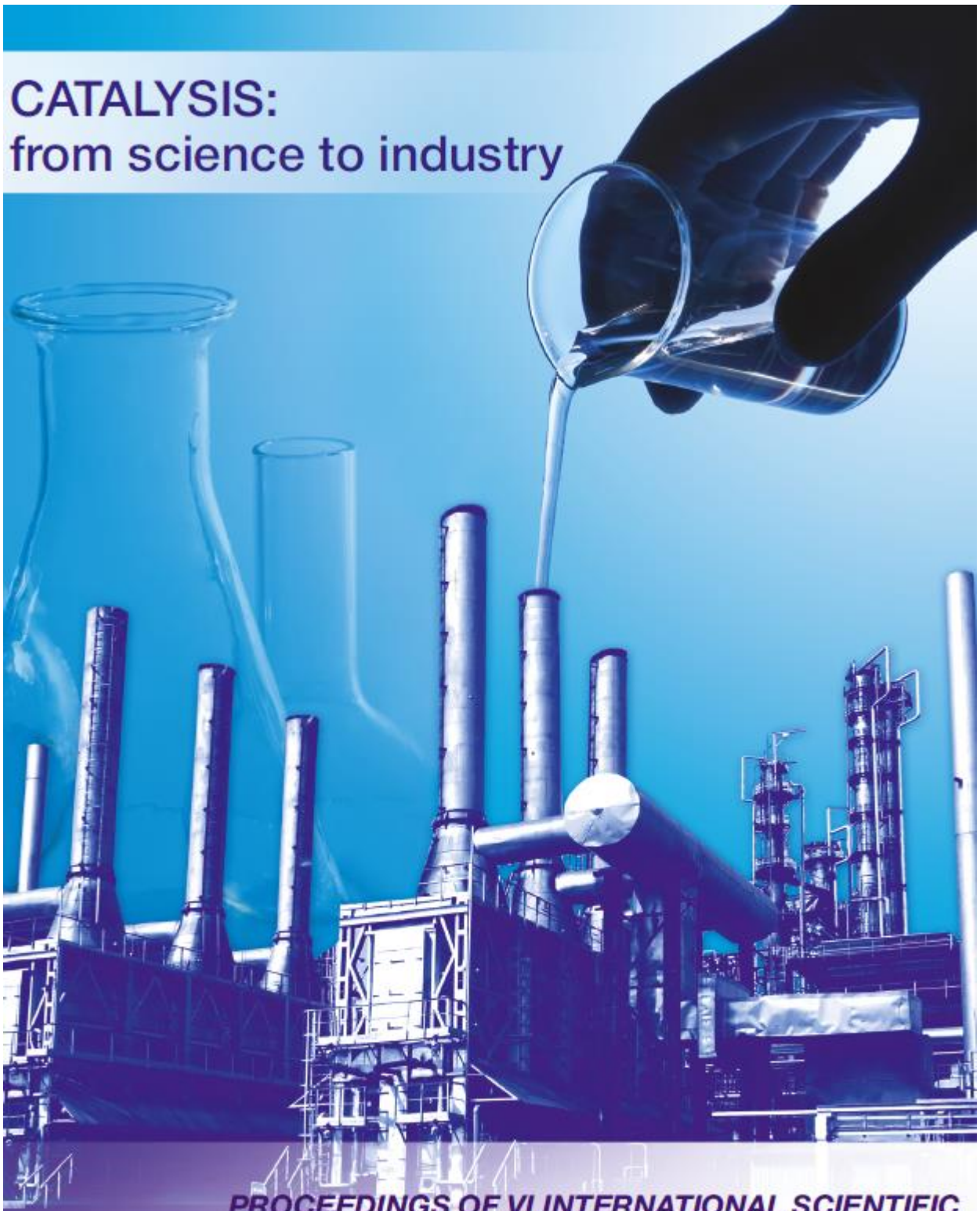
CATALYSIS:
from science to industry



PROCEEDINGS OF VI INTERNATIONAL SCIENTIFIC SCHOOL-CONFERENCE FOR YOUNG SCIENTISTS

October 6-10, 2020
Tomsk State University, Tomsk

THE MINISTRY OF EDUCATION AND SCIENCE OF THE RUSSIAN FEDERATION
NATIONAL RESEARCH TOMSK STATE UNIVERSITY

CATALYSIS: FROM SCIENCE TO INDUSTRY

Proceedings of
VI International scientific school-conference for young scientists

October 6-10, 2020

Tomsk 2020

UDC 544.47/544.72+661.7
LBC 24.54
P75

P75 **Catalysis: from science to industry:** Proceedings of VI International scientific school-conference for young scientists "Catalysis: from science to industry" / Tomsk State University. – Tomsk: "Ivan Fedorov" publishing, 2020. – 108 p.

ISBN 978-5-91701-145-5

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.

UDC 544.47/544.72+661.7
LBC 24.54

Alcohol effect on the catalytic properties of CuO_x water-ethanol colloids obtained by laser ablation in 4-nitrophenol hydrogenation

D.A. Goncharova, T.S. Kharlamova, O.A. Reutova, V.A. Svetlichnyi

[1]*Tomsk State University, Tomsk, Russia*

dg_va@list.ru

Currently, great attention is paid to the catalytic reduction of nitro compounds, in particular 4-nitrophenol (PNP), with sodium borohydride ($NaBH_4$) representing an effective and environmentally friendly reducing agent. In this reaction the catalysts based on noble (Pt, Ag, Au, Pd) and transition (Co, Fe, Ni, Mn, Cu) metals are used. The Cu-containing catalysts are less expensive and potentially can be selective, while the catalytic characteristics are comparable to those of nanocatalysts based on noble metals [1]. A rapidly developing and promising method to prepare the catalytically active surfactant-free colloidal nanoparticles is pulsed laser ablation in a liquid (LAL) [2]. We have recently shown that CuO_x NPs with various phase composition (Cu, Cu_2O, Cu@Cu_2O), sizes and morphology are formed by LAL of copper in water and ethanol [3]. In this work, the LAL of copper in water-ethanol solution was carried out and the catalytic activity of the obtained colloids was investigated in the PNP hydrogenation with $NaBH_4$.

CuO_x NPs dispersions (40-60 mg/l) were prepared by the LAL of copper in distilled water, ethanol and water-ethanol solution (10, 20, 30, 50, 70%wt. of ethanol) according to the technique described in Ref. [3]. The prepared samples were characterized by XRD (XRD6000, Shimadzu (Japan)), UV–vis absorption spectroscopy (Cary100, Varian (Australia)), and TEM (CM 12, Philips (Netherlands)). The catalytic properties of the obtained CuO_x NPs in PNP reduction were studied using aqueous solutions of PNP and $NaBH_4$ at 19 °C. Typically, 1.7 ml of distilled water, 200 μl dispersion of CuO_x NPs (15 mg/l) aged for 3 days and 300 μl of freshly prepared $NaBH_4$ aqueous solution (5×10^{-2} mol/l) were mixed at a rate of 300 rpm during 2 min and added to 300 μl of the PNP aqueous solution (2.57×10^{-4} mol/l). The reaction was performed inside the quartz cuvette (10 mm), and the reduction processes were monitored online by following the PNP optical absorption peak at 400 nm with 10 s intervals using CM 2203 spectrophotometer (SOLAR (Belarus)).

As a result, the composition of the used water-ethanol solution in the studied range of alcohol concentration from 10% to 70% was shown to affect the size of the resulting particles and the sedimentation stability of the obtained sols, but did not significantly affect the phase composition of the particles obtained during the LAL as well as changing of their phase composition and morphology during the sol aging.

The results of the catalytic studies of CuO_x NPs in sols obtained by LAL indicated their high activity in the PNP reduction comparable to or higher than the one of CuO_x-based catalysts obtained by other methods. An increase in the alcohol concentration in the reaction medium was shown to generally increase the induction period and decrease the effective reaction rate constant. It has been determined that the alcohol effect on the kinetics of PNP reduction was found to be due to the alcohol adsorption on the catalyst surface that was well described within the framework of the Langmuir-Hinshelwood kinetic model. The alcohol presented in the reaction medium showed an inhibitory effect on the process of substrate reduction due to the alcohol sorption on the same sites of the catalyst surface along with the reagents.

This work was supported by the Tomsk State University competitiveness improvement programme.

References

1. Prucek, R.; Kvítek, L.; Panáček, A.; Vančurová, L.; Soukupová, J.; Jančík, D.; Zbořil, R. *J. Mater. Chem.* **2009**, *19* (44), 8463–8469.
2. Reichenberger, S.; Marzun, G.; Muhler, M.; Barcikowski, S. *ChemCatChem* **2019**, *11* (18), 4489–4518.
3. Goncharova, D.A.; Kharlamova, T.S.; Lapin, I.N.; Svetlichnyi, V.A. *J. Phys. Chem. C* **2019**, *123*, 21731–21742.