

Catalytic investigation of Pd-graphite oxide nanocomposites

Tamás Szabó^{1*}, Ágnes Mastalir², Imre Dékány²

¹Department of Physical Chemistry and Materials Science, University of Szeged, H-6720 Szeged, Aradi vértanúk tere 1, Hungary

²Department of Organic Chemistry, University of Szeged, H-6720 Szeged, Dóm tér 8, Hungary

*e-mail: sztamás@chem.u-szeged.hu

Graphite-oxide (GO) is a layer-structured material, produced by the controlled oxidation of graphite. In contrast to pristine graphite, the GO lamellae contain hydroxyl and epoxide functional groups on their basal planes, in addition to carbonyl and carboxylic groups located at the sheet edges. The presence of these functional groups makes the graphene oxide sheets strongly hydrophilic. As a result, GO readily adsorbs water and other polar liquids and exhibits one-dimensional swelling, similarly to clay minerals [1,2]. GO is a two-dimensional solid, with strong covalent bonding within the layers and weaker interlayer contact between intercalated water molecules. GO readily undergoes disaggregation and has an excellent intercalation ability and cation exchange capacity. The favourable properties of GO make it particularly suitable for application as a host material of catalytically active metal nanoparticles [3]. Cationic surfactant-GO nanocomposites have been synthesized via reactions between aqueous solutions of surfactants and colloidal GO suspensions. Various kinds of surfactants were intercalated into GO and their structures were investigated [4].

In the present study, hydrophobic GO nanocomposites were synthesized and applied as host materials of monodispersed Pd nanoparticles. GO was prepared according to Brodie's method. Low-loaded organophilic Pd-GO nanocomposites were synthesized in micellar systems, by using the precursor K_2PdCl_4 and the aqueous solution of the cationic surfactant tetradecylammonium bromide ($C_{14}TAB$) as a stabilizer. Reduction of the precursor was performed by an excess of $NaBH_4$, which resulted in the formation of a stable Pd sol. The Pd particles were surrounded by a protective layer of the cationic surfactant molecules. Upon mixing the Pd sol with an aqueous GO suspension, the surfactant molecules were released from the surface of Pd and irreversibly bound to the cation exchanger positions of GO. Simultaneously, the Pd particles were immobilized on the surface of the GO lamellae via adhesion. The amount of surfactant cations on the surface sites of GO was equal to its cation exchange capacity. The surfactant cations made the surface of GO hydrophobic, which ensured that Pd-GO could be readily dispersed in organic solvents. The Pd-GO nanocomposites were characterized by ICP-AES, XRD and TEM measurements. The catalytic performances of the samples were investigated in an automated hydrogenation reactor, for the liquid-phase hydrogenations of terminal and internal alkynes under mild conditions (101325 Pa, 298 K). The hydrogen consumption was recorded as a function of reaction time. The reaction rates were determined from the slopes and the turnover frequencies (TOF) were calculated. Experimental results indicated that the Pd/GO samples were highly active and selective catalysts for alkyne hydrogenations. It was also established that a considerable proportion of the particles was accommodated in the interlamellar space of GO, which was found to have a crucial effect on the catalytic behaviour.

Acknowledgements Financial support through Grant OTKA K109278 is gratefully acknowledged.

- [1] S. Stankovich, D.A. Dikin, G.H.B. Dommett, K.M. Kohlhaas, E.J. Zimney, E.A. Stach, R.D. Piner, S.T. Nguyen, R.S. Ruoff, *Nature*, 2006, **442**, 282.
- [2] I. Dékány, R. Krüger-Grasser, A. Weiss, *Colloid Polym. Sci.* 1998, **276**, 570.
- [3] Á. Mastalir, Z. Király, M. Benkő, I. Dékány, *Catal. Lett.* 2008, **124**, 34.
- [4] Y. Matsuo, T. Niwa, Y. Sugie, *Carbon* 1999, **37**, 897.