

ORIGINAL PAPER

Role of polyaniline morphology in Pd particles dispersion. Hydrogenation of alkynes in the presence of Pd-polyaniline catalysts

^aRobert Kosydar, ^aMonika Goral, ^aAlicja Drelinkiewicz*, ^bJaroslav Stejskal

^a*Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Kraków, Poland*

^b*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic,
Heyrovsky Sq. 2, 162 06 Prague, Czech Republic*

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Two polyaniline (PANI) samples of various molecular masses were used for the preparation of palladium catalysts (with 2 mass % of Pd). The physicochemical features of starting polyanilines were found to substantially affect the size and extent of palladium nanoparticles aggregation. Strongly aggregated large palladium particles appeared in the PANI sample of more compact morphology (PANI-H), higher crystallinity and lower specific surface area. Pd nanoparticles of a definitively smaller size were formed in the more amorphous PANI sample of looser morphology (PANI-L) and the extent of particles aggregation was markedly lower. The catalytic properties of Pd/PANI samples were studied in a liquid phase hydrogenation of unsaturated triple bond ($C\equiv C$) in alkynes reactants, phenylacetylene, and cyclohexylacetylene. The 2 mass % Pd/PANI-L catalyst prepared using polymer of less compact texture exhibited much higher activity in both reactions. In the presence of the 2 mass % Pd/PANI-L catalyst, alkene products were formed with a high selectivity (approximately 90 %) attained at the almost complete conversion of alkynes. This highly selective hydrogenation of the $C\equiv C$ to the $C=C$ bond was related to the presence of an electroactive polymer, PANI, in close proximity with Pd active sites. Polyaniline could have a role in a steric effect as well as in a modification of adsorptive properties of Pd centres.

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Introduction

Polyaniline (PANI) is one of the conductive polymers studied most extensively due to its environmental stability, controllable electrical conductivity and interesting chemical properties (Kang et al., 1998). PANI undergoes protonation with acids to afford the conducting “salt”; the polymer also readily participates in redox reaction. Both these processes have been involved in the synthesis of PANI-transitions metals composites. Nitrogen groups, particularly the imine ($-N=$) ones, could also be considered as potential centres for the coordination of metal ions, such as Ag, Cu, Pd. In the interaction with metal, the system of π -conjugated bonds could be involved (Kumar

et al., 1995). Unpaired electrons and positive charges delocalised over the entire conjugation length of the PANI could provide an environment similar to a π -donor ligand (Hirao, 2002; Higuchi et al., 1996; Kumar et al., 1995). Electron interactions between PANI and palladium nanoparticles resulted in a change in the reduction–oxidation properties of PANI examined by the cyclic voltammetry technique (Park et al., 2004). These interactions were also predicted by theoretical calculations performed by quantum chemistry methods (Białek, 2006). In the light of these observations, it might be expected that the PANI matrix could influence the reactivity of Pd-centres in a catalytic reaction. This phenomenon was observed for palladium–polypyrrole catalysts (Drelinkiewicz et al.,

*Corresponding author, e-mail: ncdrelin@cyf-kr.edu.pl