

ORIGINAL PAPER

Effect of support on activity of palladium catalysts in nitrobenzene hydrogenation

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The effect of two types of catalysts on the activity of the catalytic hydrogenation of nitrobenzene was studied. Catalysts were prepared by the surface deposition of palladium hydroxide with a simultaneous reduction with formaldehyde in a basic environment and were characterised by X-ray powder diffraction, transmission electron microscopy, adsorption–desorption, and catalytic tests – hydrogenation of nitrobenzene in methanol. The influence of the supports' (activated carbon and a mixture of activated carbon and multi-walled carbon nanotubes) surface area is discussed. Despite having a size comparable (4–5 nm) to crystallites of metallic palladium, the catalyst prepared on a mixture of activated carbon and nanotubes (Pd/C/CNT) was significantly less active than the catalyst prepared on pure activated carbon (Pd/C); the rate of this reaction was approximately 30 % lower than the initial reaction rate. This feature could be attributed to the lower specific surface area of the Pd/C/CNT (531 m² g⁻¹) in comparison with the Pd/C (692 m² g⁻¹). (c) 2013 Institute of Chemistry, Slovak Academy of Sciences

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Introduction

The catalytic hydrogenation of nitrobenzene (NB) is important in the industrial production of aniline (AN). This process has been the subject of studies over a long period (Kolbe, 1871; Saytzeff, 1872) and many books and papers refer to the methods for the preparation of Pd catalysts on different carriers which influence the process of hydrogenation (Nishimura, 2001; Campanati et al., 2003; Zaitseva et al., 2011; Belykh et al., 2006; Bianchi et al., 1997; Obraztsova et al., 2008; Udayakumar et al., 2011; Wan et al., 1998). The usual preparation procedures include the deposition of the active metal and its reduction, leading to the formation of metallic palladium on the surface of the carrier (Semikolenov, 1992). Different types of carbon materials (Harada et al., 2007) and activated carbon (AC) (Bouchenafa-Saïb et al., 2005; Gelder et al., 2002; Ma et al., 2011; Watanabe & Arunajatesan, 2010) have been used as supports for palladium because of the large internal surface area, which ensures a high dispersion of the metallic palladium; as a consequence, a high specific catalytic activity of the dispersed metallic palladium is expected.

AC was used as a support for palladium in the liquid-medium hydrogenation of NB to AN. Even after the oxidising treatment of AC, the dispersion of 5 mass % of Pd on the support exhibited high activity (Bouchenafa-Saïb et al., 2005). Nanostructured catalyst supports, such as carbon nanofibres (CNF)

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