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Novel microwave synthesis of ruthenium nanoparticles supported on carbon nanotubes active in the selective hydrogenation of p-chloronitrobenzene to p-chloroaniline

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ABSTRACT

Carbon nanotubes (CNTs) have been employed for the preparation of supported ruthenium nanoparticles using, for the first time, a low boiling alcohol or a mixture ethanol/water as solvent/reducing agent under microwave irradiation as heating source. These systems were employed as catalysts in the selective hydrogenation of p-chloronitrobenzene (p-CNB) to p-chloroaniline (p-CAN) and resulted efficient systems for the selective reduction of the nitro group in p-CNB under mild reaction conditions (60 °C and 4 MPa of H_2), while the C—Cl bond remains intact, thus allowing the almost complete substrate conversion with total selectivity to the target product. These supported ruthenium nanoparticles are characterized by small average diameters and narrow particle size distributions, even if synthesized in the absence of any additional stabilizing agents and appear very promising systems also for other catalytic applications.

1. Introduction

The role of catalysis in the development of clean chemical production with limited hazardous and toxic by-products is now well-established as an essential element of sustainable processing [1]. Today, aromatic haloamines are extensively employed as intermediates in the manufacture of many fine chemicals [2,3]. In particular, p-chloroaniline is applied as curing agent for epoxy resins, as cross-linking agent in some polymer preparations and in pharmaceuticals for the synthesis of tranquilizers [4]. These organic amines are currently produced through the reduction of the corresponding aromatic halonitro compounds either by Bechamp's reaction, using a metal–acid reduction system, or by selective hydrogenation over transition-metal catalysts. The former stoichiometric method has been falling into disuse in industry because it produces a great amount of Fe/FeO sludge which cannot be recycled, thus causing a serious environmental pollution [5]. The second route is characterized by a clean production process, high atom economy, cheap operations, easy product separation and can offer high selectivities to the desired product with a significantly lower environmental impact [6]. However, it is still difficult to industrially apply this process because of the extensive dechlorination which lowers the selectivity, producing also corrosive hydrogen chloride [7]. A number of reaction parameters have been shown to affect the activity and the selectivity to chloroanilines, but the secondary dechlorination reaction cannot be completely avoided [8]. Many studies regarding this hydrogenation reaction have been made both in gas [9,10] and in liquid phase [11–16], emerging the last as the cleanest and the most sustainable alternative. Most researches were focused on heterogeneous metal catalysts [11–26], such as Pd [17], Pt [11,12,18,19], Rh [20], Ir [13,21], Ni [14], Raney Ni [22], Au [15], Ru [10,16,23–29] and poly-metallic catalysts [30]. Palladium catalysts are the more widely employed, but though they show high activities, the selectivity to chloroaniline remains low because of the dehalogenation reaction [17,31]. Platinum based catalysts have been also deeply investigated: although they show interesting catalytic performances under mild reaction conditions, now they are not suitable for an industrial expansion due to the high price of platinum [32]. Very few attempts were performed using rhodium and iridium catalysts which, despite promising selectivities, are scarcely active [21]. Well-investigated catalysts were also nickel ones because of their acceptable cost compared to other noble

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