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Journal of Molecular Catalysis A: Chemical 230 (2005) 97–105
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
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Catalytic activity of palladium supported on single wall carbon nanotubes compared to palladium supported on activated carbon Study of the Heck and Suzuki couplings, aerobic alcohol oxidation and selective hydrogenation

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Received 30 September 2004; received in revised form 29 November 2004; accepted 29 November 2004
Available online 21 January 2005

Abstract

Nanoparticles (2–10 nm) of palladium have been deposited on single wall carbon nanotubes (SWNT) by spontaneous reduction from $Pd(OAc)_2$ or from oxime carbapalladacycle. These catalysts exhibit higher catalytic activity than palladium over activated carbon (Pd/C) for the Heck reaction of styrene and iodobenzene and for the Suzuki coupling of phenylboronic and iodobenzene. This fact has been attributed as reflecting the dramatic influence of the size particle on the activity of the palladium catalyst for C─C bond forming reactions as compared to other reaction types less demanding from the point of view of the particle size. Thus, in contrast to the Heck and Suzuki reactions, Pd/C is more active than palladium nanoparticles deposited on SWNT for the catalytic oxidation by molecular oxygen of cinnamyl alcohol to cinnamaldehyde and for the hydrogenation of cinnamaldehyde to 3-phenylpropionaldehyde.

Keywords: Nanotubes; Palladium; Single wall carbon nanotubes; Catalysts; Hydrogenation

1. Introduction

Since their discovery by Iijima [1,2], there has been a considerable interest in exploring the applications of the remarkable structural, physical and chemical properties of single wall carbon nanotubes (SWNT) in all areas of physics and material chemistry. Most of the efforts have been focused on nanotechnology trying to exploit the mechanical strength [3–5] and metallic conductivity [5–10] of different kinds of SWNT as well as the possibility to functionalize covalently SWNT to obtain advanced materials [11–13].

SWNT have also been used in heterogeneous catalysis as support for noble metals [14–18]. The reports on the use of SWNT in catalysis are, however, considerably more scarce than those focused on material science and more effort is still necessary to assess the performance of SWNT, particularly compared to widely used activated carbons. We have been involved in the use of SWNT as solid supports for catalytic reactions [19]. Our interest comes from the consideration of the importance that activated carbons have as optimum supports for many reaction types including catalytic hydrogenations and oxidations. In both cases, the known ability of SWNT to adsorb gases in even higher quantities than activated carbons might be advantageous co-operating to the success of the reaction. For instance, given that the interior of the tubes is open to the exterior, there has also been a large interest in the use of SWNT for hydrogen storage [20–27].

SWNTs are, however, structurally and chemically very different from most activated carbons. SWNT have a well-defined structure formed by thin (1.3 nm) and long (>100 nm) carbon tubes of remarkable flexibility, mechanical strength and high Young modulus that agglomerate through van der Waals forces to form bundles. Purified SWNTs free from

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doi:10.1016/j.molcata.2004.11.030

catalyst particles [14] are formed by an almost perfect graphene wall terminated with carboxy groups. In contrast to this remarkable periodicity, activated carbons have ill-defined structures constituted of a wide distribution of platelets of condensed aromatic hydrocarbons of different sizes and compositions connected through methylene, oxygen, nitrogen or sulfur bridges. Also depending on the source of the activated carbons, significant percentages of heteroatoms (O, N, S) and even transition metals can be present in activated carbons forming a large variety of functional groups such as phenol, quinones and sulphonic.

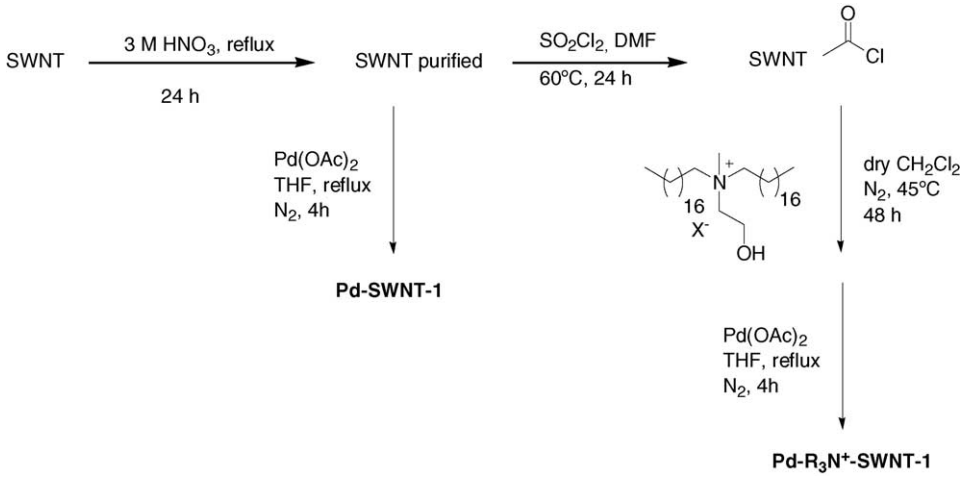
In the present work, we want to report the catalytic activity of palladium metal-containing SWNTs prepared by three different procedures for a series of palladium catalyzed reactions, namely the Heck and Suzuki C–C coupling, alcohol aerobic oxidation and C=C hydrogenation. Our goal is to compare the results obtained with palladium-supported SWNT with those achieved with Pd/C to establish differences on the performance between both catalysts for a series of catalytic reaction that might exhibit different demand from the point of view of particle size. Our results show indeed that the catalytic activity of palladium on SWNT exhibits a characteristic pattern that is clearly different from that of Pd/C, the former system being specially interesting from C–C cross-coupling reactions, for which palladium particle size seems to play a crucial role compared to hydrogenations and oxidations.

2. Results and discussion

2.1. Preparation of palladium catalysts supported on SWNT

Metal nanoparticles exhibit specific properties arising from the large surface/bulk atomic ratio. These properties are not observed in larger micrometric or submicrometric particles in where the fraction of external atoms is negligible with respect to the number of internal atoms [28,29]. From the recent work on metal nanoparticles, it has become evident that the catalytic activity of a palladium containing catalysts depends on a large extent of the particle size, on the dispersion of the nanoparticles and on the way in which nanoparticles are stabilized against agglomeration [30–32]. Some of these properties are determined by the preparation procedure and controlled in a certain extent by the support. The preparation procedure is crucial to obtain particles of the nanometric size with adequate stability and dispersion. In the present work, we have prepared three types of SWNT supported palladium metal catalysts in where two precursors of the palladium metal have been used or in where the SWNT has been conveniently functionalized to introduce a covalently bonded quaternary ammonium stabilizer [33].

A commercial sample of HiPCO single wall carbon nanotube normally contains rest of the solid catalyst particles used for the synthesis of the SWNT from organic molecules. The typical purification procedure consists on treating the SWNT sample with concentrated aqueous solution of nitric acid at 100 °C for long times. After purification, the absence of catalyst particles can be simply assessed by thermogravimetric analysis (TGA) where the complete burning of the material should be observed and also by elemental analysis in where a high C content should be measured. In our case, TGA after purification shows no residue and at the same time the chemical analysis of ambient-equilibrated purified SWNT (still containing some humidity) show a carbon content about 80%, the remaining percentage being attributed to adsorbed water from the ambient. The simplest preparation procedure consists in contacting SWNT with a solution of palladium acetate. In the literature, it has been reported that upon contacting platinum or gold salts with SWNT a spontaneous reduction occurs forming the corresponding metal nanoparticles distributed along the carbon nanotubes [34]. A electrochemical current can be measured during the reduction. Although we have not been able to find an analogous report using palladium salts, it could be easily anticipated



Scheme 1. Synthetic route followed to obtain the SWNT-supported palladium catalyst Pd-SWNT-1 and Pd-R_3N^+-SWNT-1.