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Size-Selective, Stabilizer-Free, Hydrogenolytic Synthesis of Iridium Nanoparticles Supported on Carbon Nanotubes

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Supporting Information

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The synthesis of catalytically active, inorganic nanoparticles (NPs) with a high degree of control on particle size and shape has gained significant interest in recent years. Shape and especially the size of nanocrystals are of major importance for the chemical and physical properties of the material.[1−9] Nanocrystals are most often prepared using either reductive or thermolytic conditions in solutions and require surfactants or stabilizing agents to prevent nanoparticle agglomeration. Additionally, various borane complexes are utilized as reductants but risk poisoning the nanoparticles. For thermolysis, metal carbonyls are the most readily available precursors, since the metal is already present in M(0) oxidation state.[10−12] However, metal carbonyls can be hazardous due to their toxicity. Furthermore, strict exclusion of water and air is necessary. Apart from thermolytic processes for the generation of metal nanoparticles, ultrasound is another method for their preparation.[3] In addition, ionic liquids (ILs) provide a convenient medium for the generation of nanoparticles.[4] However, ILs may interact with NPs and thus poisoning of the latter cannot always be dismissed.[17] Furthermore, unfavorable interaction between the substrate and ILs may occur. We became interested in a new, convenient method for the preparation of nanocrystals on solid support, circumventing the aforementioned hazards or difficulties. In particular, we were seeking a heterogeneous catalyst system for the efficient reduction of N-heterocycles.

Iridium[13−30] is the most commonly used catalyst for the reduction of imines to the corresponding amines, which are important building blocks for pharmaceuticals or agrochemicals. Many different applications have been developed over the past decades using iridium catalysts for homogeneous hydrogenations of imines as well as *N*-heterocycles.[31,32] In contrast to homogeneous catalysts, which suffer from extra ligand synthesis and which often cannot be reused or reisolated after use, heterogeneous catalysts offer the benefit of easy recycling. Moreover, using continuous flow processes the substrate can be easily passed over such catalysts and the product can be collected without the need for further purification. However, no chemoselective, heterogeneous catalyst for the selective hydrogenation of quinolines has been reported to date. The reason is that, for instance, readily available Pd/C or Rh/C suffers from the over reduction of the [H_4]-quinoline to the [H_{10}]-quinoline.[33,34] Therefore, a convenient method for the preparation of new, chemoselective catalysts is of great interest for the development of new and efficient approaches to tetrahydroquinolines and other *N*-heterocylces.

We were interested in a hydrogenolytic approach to nanoparticles.[9,14] With only molecular hydrogen present, the only concomitant impurity may be metal-hydrides formed during the hydrogenation process. To prevent a sintering of nanoparticles, we had to substitute the stabilizers with a different solid support, holding the precursor molecules apart from each other and thus minimizing the risk of uncontrolled nanoparticle agglomeration. In seeking a suitable material for this purpose, we investigated carbon nanotubes. They should provide first a solid support, and second a matrix to prevent nanocrystals from diffusing and then agglomerating. Among the different types of carbon materials, carbon nanotubes (CNTs) offer significant advantages over other carbon supports, including carbon nanofibers (CNFs), graphenes or graphite.[35−47] CNTs can be synthesized with high-purity, which lowers the risk of self-poisoning. Moreover, they possess outstanding mechanical properties and are stable over a wide temperature range. The catalytically active phase of CNTs is easily accessible and due to the fact that CNTs possess no microporosity, potential substrates do not have to diffuse into small pores, but can react on the readily accessible surface of CNTs. Thus CNTs represent an interesting alternative to conventional carbon-based solid supports.

To date, CNT-supported heterogeneous iridium catalysts have been mainly employed in hydrogenation reactions of cinnamic aldehyde,[37−39] hydroformylations,[41] Fischer−Tropsch reactions[43] or in photo-[44] and electrocatalysis.[45,46] The fact that CNTs are inert to acidic or basic media makes them an optimal heterogeneous support for the reduction of acyclic or cyclic imines. However, CNTs are frequently pretreated with nitric acid to perform a functionalization of the surface. Via this treatment carboxyl-groups and carboxylic-anhydrides are formed on the surface which are claimed to have beneficial effects for the formation of nanoparticles.[38] Yet, in the context of the reduction of basic imines this functionalization of CNTs may be a major drawback as the product can easily bind to the surface, either through ion pairing or amide formation. Therefore, we decided

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Scheme 1. Preparation of Iridium-Coated Carbon Nanotubes

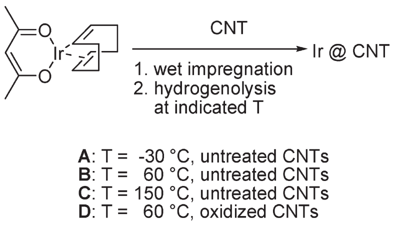
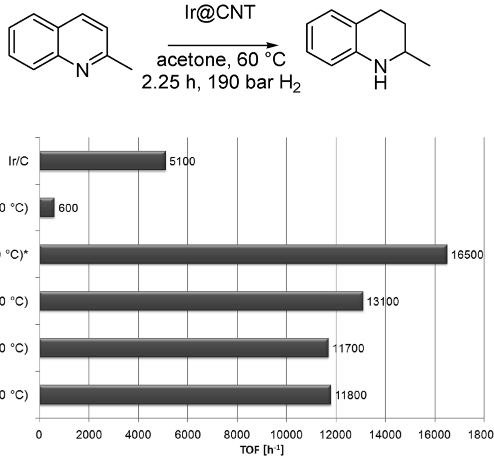


Table 1. Reactivity of Iridium on CNT



General reaction conditions: TOF calculated from conversion (by GC-FID), substrate/catalyst = 30.000, reaction time 2.25 h. * substrate/catalyst = 200.000, reaction temperature 150 °C, reaction time 12h.

to use untreated CNTs as a solid support for preparing iridium nanoparticles for reduction of different N-heterocycles.

We started our investigations with the synthesis of iridium-coated carbon nanotubes (see Scheme 1) using an adsorption-hydrogenolysis approach. Applying Ir(cod)acac as the metal precursor we performed a wet adsorption on CNTs by slowly removing the dichloromethane solvent. The formation of NPs is often dependent on the nucleation rate, which can be correlated to the hydrogenolysis temperature. Thus, we examined the formation of Ir@CNT at different temperature under a set pressure of 150 bar and subsequently used these newly generated catalysts in the reduction of quinaldine.

Interestingly, the temperature of the hydrogenolysis had a significant impact on the subsequent evaluation of the catalytic activity of the heterogeneous iridium catalyst. While an almost inactive iridium catalyst **A** was obtained when the hydrogenolysis was performed at −30 °C, highly reactive catalysts **B**, **C**, and **D** were obtained, if the hydrogenolysis was carried out at 60 and 150 °C, respectively. Oxidative treatment of CNTs only has a small effect on the catalyst reactivity. Turnover numbers (TON) for the latter three catalysts were calculated to be about 29.000 and 27.000, with a turnover frequency (TOF) exceeding 11.000 h^{-1} (see Table 1). This is to date the highest TOF reported for the hydrogenation of quinolines. Compared to analogously prepared Ir/C, the reactivity of Ir/CNT is 2.5 to 4 times higher and clearly underlines the effectiveness of the CNT support.

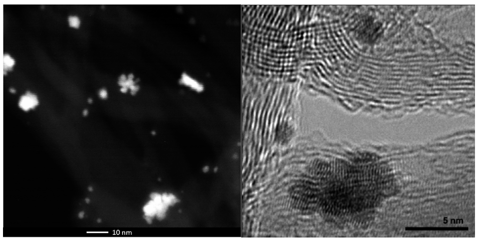


Figure 1. STEM/HRTEM investigation of sample B. (a) Brighter areas in the ADF-STEM image marks the location of metal particles. (b) Corresponding HREM image taken from this area shows lattice fringes from crystalline iridium particles and the CNT support.

To gain further insight into the nature of the catalytic active component of the heterogeneous catalysts the samples were examined by high-resolution transmission electron microscopy (HRTEM) and annular dark field (ADF) scanning transmission electron microscopy (STEM), respectively. Additionally, we carried out energy dispersive X-ray spectroscopy (EDX) which provides important information of the chemical composition of the iridium coated nanotubes with lateral resolution on the nanometer scale. As indicated by the hydrogenation experiments, the temperature of the hydrogenolysis reaction showed a significant influence on the size and distribution of the iridium nanoparticles. TEM investigation of sample A proves that hydrogenolysis at −30 °C yields a CNT support that is virtually free from iridium metal particles.[48] However, TEM-EDX measurements give evidence for small amounts of iridium being present in the material, most probably in the form of microfilms.

Increasing the temperature of the hydrogenolysis to 60 °C resulted in the formation of iridium nanoparticles, dispersed on carbon nanotubes (sample B). Although STEM images show formation of nanoparticles in the range between about 1 to 20 nm, HRTEM images reveal that the larger particles are agglomerations of smaller nanoparticles (Figure 1). This was also proven by inspecting different orientation of crystalline nanoparticles in the bulkier agglomerates.

Further increase of the hydrogenolysis temperature to 150 °C (sample C) yielded finely dispersed nanocrystals in the size range of 1−10 nm on CNT without formation of larger agglomerates. The crystalline nature of the nanoparticles was again shown by HRTEM imaging.

Investigations of sample **D** by transmission electron microscopy revealed the nature of the effect of the oxidative treatment of CNTs toward the formation of iridium nanoparticles under hydrogenolytic conditions. The particle size distribution is very similar to sample **C** that was prepared on untreated CNTs at 150 °C. As observed for sample **C**, only very few agglomerates of iridium nanocrystals can be found in sample **D**. This indicates that a high control over the preparation of iridium nanoparticles supported on CNTs can either be achieved by high temperature hydrogenolysis or by oxidative treatment of CNTs prior to the hydrogenolysis.

In accordance with this finding, the reactivity toward the reduction of quinaldine is very similar (11.700 h^{-1} for sample **C** and 11.800 h^{-1} for sample **D**, respectively).

The above findings can be rationalized by a mechanism in which the nucleation of the nanoparticles plays the dominant role. At low temperatures, nucleation is slow and thus intermediate iridium species during nanoparticle formation can diffuse or move on the surface of CNTs and get reduced only in the event of collision with an existing nucleation seed. This results in larger microparticles or microfilms, which are catalytically less active. At high temperatures, fast nucleation is favored, numerous nuclei are being formed, and thus smaller nanoparticles are observed.

Herein we describe the synthesis of iridium nanoparticles on both functionalized and unfunctionalized carbon nanotubes, using for the first time a stabilizer-free, hydrogenolytic approach for nanoparticle formation. Both the temperature of the hydrogenolysis and the oxidative pretreatment play important roles in the preparation of the nanoparticles that are formed in a nucleation-limited pathway. Although at low temperature nucleation is slow and large particles are formed, the use of high temperatures during the hydrogenolysis process favors the formation of highly reactive iridium nanoparticles. The Ir@CNT catalyst formed by this method not only exhibits the highest catalytic activity in batch reduction of *N*-heterocycles[48] to date but it can additionally be employed in continuous flow reductions.[48] Further research is directed to a better understanding of the nanoparticle formation employing different metal precursors as well as further investigations toward applications in catalysis.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional TEM, SEM, STEM, and HRTEM images; experimental and synthesis details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Finney, E. F.; Finke, R. G. *J. Colloid Interface Sci.* **2008**, *317*, 351–374.

(2) Tao, A. R.; Habas, S.; Yang, P *Small* **2008**, *3*, 310–325.

(3) Bang, J. H.; Suslick, K. S *Adv. Mater.* **2010**, *22*, 1039–1059.

(4) Dupont, J.; Scholten, J. D. *Chem. Soc. Rev.* **2010**, *39*, 1780–1804.

(5) Ott, L. S.; Finke, R. G. *Coord. Chem. Rev.* **2007**, *251*, 1075–1100.

(6) Cozzoli, P. D.; Pellegrino, T.; Manna, L. *Chem. Soc. Rev.* **2006**, *35*, 1195–1208.

(7) Migowski, P.; Dupont, J. *Chem.—Eur. J.* **2007**, *13*, 32–39.

(8) Migowski, P.; Zanchet, D.; Machado, G.; Gelesky, M. A.; Texeira, S. R.; Dupont, J. *Phys. Chem. Chem. Phys.* **2010**, *12*, 6826–6833.

(9) Mondloch, J. E.; Wang, Q.; Frenkel, A. I.; Finke, R. G. *J. Am. Chem. Soc.* **2010**, *132*, 9701–9714.

(10) Silva, D. O.; Scholten, J. D.; Gelesky, M. A.; Teixeira, S. R.; Dos Santos, A. C. B.; Souza-Aguiar, E. F.; Dupont, J. *ChemSusChem* **2008**, *1*, 291–294.

(11) Vollmer, C.; Redel, E.; Abu-Shandi, K.; Thomann, R.; Manyar, H.; Hardacre, C.; Janiak, C. *Chem.—Eur. J.* **2010**, *16*, 3849–3858.

(12) Redel, E.; Krämer, J.; Thomann, R.; Janiak, C. *J. Organomet. Chem.* **2009**, *694*, 1069–1075.

(13) Ott, L. S.; Finke, R. G. *Chem. Mater.* **2008**, *20*, 2592–2601.

(14) Bayram, E.; Zahmakiran, M.; Özkar, S.; Finke, R. G. *Langmuir* **2010**, *26*, 12455–12464.

(15) Özkar, S.; Finke, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 4800–4808.

(16) Lin, Y.; Finke, R. G. *Inorg. Chem.* **1994**, *33*, 4891–4910.

(17) Ott, L. S.; Campbell, S.; Seddon, K. R.; Finke, R. G. *Inorg. Chem.* **2007**, *46*, 10335–10344.

(18) Bernardi, F.; Scholten, J. D.; Fecher, G. H.; Dupont, J.; Morais, J. *Chem. Phys. Lett.* **2009**, *479*, 113–116.

(19) López-De Jesús, Y. M.; Vicente, A.; Lafaye, G.; Marécot, P.; Williams, C. T. *J. Phys. Chem. C* **2008**, *112*, 13837–13845.

(20) Özkar, S.; Finke, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 5796–5810.

(21) Park, I. S.; Kwon, M. S.; Kang, K. Y.; Lee, J. S.; Park, J. *Adv. Synth. Catal.* **2007**, *349*, 2039–2047.

(22) Uzun, A.; Gates, B. C. *J. Am. Chem. Soc.* **2009**, *131*, 15887–15894.

(23) Jang, Y. B.; Kim, T. H.; Sun, M. H.; Lee, J.; Cho, S. J. *Catal. Today* **2009**, *146*, 196–201.

(24) Auer, E.; Gross, M.; Panster, P.; Takemoto, K. *Catal. Today* **2001**, *65*, 31–37.

(25) Vieira, R.; Pham-Huu, C.; Keller, N.; Ledoux, M. J. *Chem. Commun.* **2002**, 954–955.

(26) Bokhimi, X.; Zanella, R.; Angeles-Chavez, C. *J. Phys. Chem. C* **2010**, *114*, 14101–14109.

(27) Jiang, H.-Y.; Yang, C. F.; Li, C.; Fu, H.-Y.; Chen, H.; Li, R.-X.; Li, X.-J. *Angew. Chem., Int. Ed.* **2008**, *47*, 9240–9244.

(28) Scholten, J. D.; Ebeling, G.; Dupont, J *Dalton Trans.* **2007**, 5554–5560.

(29) Yinghuai, Z.; Chenyan, K.; Peng, A. T.; Emi, A.; Monalisa, W.; Louis, L. K.-J.; Hosmane, N. S.; Maguire, J. A. *Inorg. Chem.* **2008**, *47*, 5756–5761.

(30) Zhang, Y.; Zhang, H.; Zhang, Y.; Ma, Y.; Zhong, H.; Ma, H. *Chem. Commun.* **2009**, 6589–6591.

(31) Zhou, Y. G. *Acc. Chem. Res.* **2007**, *40*, 1357–1366.

(32) Glorius, F. *Org. Biomol. Chem.* **2005**, *3*, 4171–4175.

(33) Campanati, M.; Vaccari, A.; Piccolo, O. *J. Mol. Catal. A: Chem.* **2002**, *179*, 287–292.

(34) Campanati, M.; Casagrande, M.; Fagiolino, I.; Lenarda, M.; Storaro, L.; Battagliarin, M.; Vaccari, A. *J. Mol. Catal. A: Chem.* **2002**, *184*, 267–272.

(35) Serp, P.; Corrias, M.; Kalck, P. *Appl. Catal., A* **2003**, *253*, 337–359.

(36) Serp, P.; Castillejos, E. *ChemCatChem* **2010**, *2*, 41–47.

(37) Plomp, A. J.; Vuori, H.; Krause, A. O. I.; de Jong, K. P.; Bitter, J. H. *Appl. Catal., A* **2008**, *351*, 9–15.

(38) Solhy, A.; Machado, B. F.; Beausoleil, J.; Kihn, Y.; Gonçalves, F.; Pereira, M. F. R.; Órfão, J. J. M.; Figueiredo, J. L.; Faria, J. L.; Serp, P. *Carbon* **2008**, *46*, 1194–1207.

(39) Li, Y.; Lai, G.-H.; Zhou, R.-X. *Appl. Surf. Sci.* **2007**, *253*, 4978–4984.

(40) Khanderi, J.; Hoffmann, R. C.; Engstler, J.; Schneider, J. J.; Arras, J.; Claus, P.; Cherkashinin, G. *Chem.—Eur. J.* **2010**, *16*, 2300–2308.

(41) Gao, R.; Tan, C. D.; Baker, R. T. K. *Catal. Today* **2001**, *65*, 19–29.

(42) Castillejos, E.; Debouttière, P.-J.; Roiban, L.; Solhy, A.; Martinez, V.; Kihn, Y.; Ersen, O.; Philippot, K.; Chaudret, B.; Serp, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 2529–2533.

(43) Kang, J.; Zhang, S.; Zhang, Q.; Wang, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 2565–2568.

(44) Wang, W.; Serp, P.; Kalck, P.; Silva, C. G.; Faria, J. L. *Mater. Res. Bull.* **2008**, *43*, 958–967.

(45) Bambagioni, V.; Bianchini, C.; Marchionni, A.; Filippi, J.; Vizza, F.; Teddy, J.; Serp, P.; Zhiani, M. *J. Power Sources* **2009**, *190*, 241–251.

(46) Shan, C.-C.; Tsai, D.-S.; Huang, Y.-S.; Jian, S.-H.; Cheng, C.-L. *Chem. Mater.* **2007**, *19*, 424–431.

(47) Machado, B. F.; Gomes, H. T.; Serp, P.; Kalck, P.; Faria, J. L. *ChemCatChem* **2010**, *2*, 190–197.

(48) For details see the Supporting Information.