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Size effect of gold nanoparticles supported on carbon nanotube as catalysts in selected organic reactions

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1. Introduction

While noble metals such as palladium, platinum, or ruthenium have been widely used in the catalysis of an array of organic transformations, gold has long been regarded as a poor catalytic species. Indeed, bulk gold is virtually devoid of chemical reactivity. However, its catalytic properties are dramatically enhanced when downsized to nanoscale and nanometric forms¹⁻³ of gold have found multiple uses in fine chemical synthesis applied, for example, to selective hydrogenations, carbon-carbon bonds formation, or oxidations.^{4–7} We recently contributed to the field of supported gold catalysis by reporting a nanohybrid structure made by the assembly of gold nanoparticles on carbon nanotubes (CNT).⁸ Carbon nanotubes offer some advantages over classical support that include chemical, thermal and mechanical stability, inertness (i.e., little to no interactions with the catalyzed organic transformation), high surface area, and chemically tunable topography.⁹ The nanohybrid structure was investigated for the catalysis of various organic transformations.^{10–13} Since previous reports indicated that the size of gold nanoparticles played, in some cases, a pivotal role in

ABSTRACT

Carbon nanotube-supported gold nanoparticles of different sizes (diameter of 3 or 20 nm) were evaluated as catalysts in four selected organic transformations. The nanohybrids were shown to efficiently catalyze the investigated reactions, regardless of the size of the supported gold nanoparticles. However, some differences were observed as regards turnover frequency values although size effect turned out to be less significant when only gold surface atoms were considered.

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determining their catalytic properties,^{14–19} we sought to investigate if this were the case as regards our nanohybrid catalyst. The relationship between the size of the CNT-supported nanogold particles and the catalytic efficacy of the nanohybrid was thus explored using gold nanoparticles of two different sizes that were assembled on the surface of carbon nanotubes using a layer-by-layer approach. This strategy permitted the assembly of small (3 nm AuNP) and larger (20 nm AuNP) gold nanoparticles on coated carbon nanotubes, leading to the corresponding nanohybrid catalysts, i.e. s-AuCNT and l-AuCNT, respectively (Fig. 1). To study the size effect of the anchored gold nanoparticles on catalyzed transformations, four-model reactions were tested, that is, the oxidation of silanes, alcohols, hydroquinones, and the direct reductive amination of aldehydes.

2. Results

2.1. Nanohybrid synthesis

The nanohybrids were prepared according to the previously reported layer-by-layer method.¹⁰ Briefly, multi-walled carbon nanotubes (MWCNT) were first coated with amphiphilic nitrilotriacetic-diyne lipid (DANTA), which self-assembled into





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Fig. 1. Overview of the two catalysts and their common coated CNT precursor.

ring-like nanostructures on the nanotube surface. The nanorings were further photo-polymerized by UV irradiation to ensure better cohesion of the nanoconstruct. Cationic poly(-diallyldimethylammonium chloride) (PDADMAC) was then added, which gave rise to the second layer through electrostatic interactions. This layer provided an interface between carbon nanotubes and gold nanoparticles. In parallel, colloidal solutions of AuNP were prepared either by THPC-²⁰ (for small AuNP) or citrate-²¹ (for larger AuNP) reduction of HAuCl₄ and the particles were deposited on the doubly coated nanotube. This final assembly step provided access to s-AuCNT and l-AuCNT nanohybrids.

Statistical size distribution analysis was carried out by transmission electron microscopy (TEM) and images of the two samples indicated mean particle diameters of ca. 3 nm for s-AuCNT and ca. 20 nm for l-AuCNT (Fig. 2). The gold content of each AuCNT aqueous suspension was assessed by ICP-MS, which indicated a concentration of 3 mM for s-AuCNT and 4 mM for l-AuCNT. The metallic nature of gold was confirmed by XPS analyses. The catalytic performances of the two hybrids were thereafter investigated on the four-model reactions mentioned above.

2.2. Silane oxidation

The selective oxidation of silanes is of broad interest for the production of silicon-containing materials^{22,23} and as nucleophilic partners in organometallic cross-coupling reactions.^{24,25} Silanes can be converted to silanols using strong oxidizing agents but significant amounts of siloxanes and toxic by-products are formed. Catalytic systems involving water combined to oxygen have recently been devised to cleanly produce silanols. Amongst heterogeneous catalysts for silane oxidation, recent examples include nanoporous gold,²⁶ hydroxyapatite-supported gold nanoparticles,²⁷ and our AuCNT nanohybrid.¹⁰

Dimethylphenyl silane (1) was chosen as a model substrate and its oxidation into the corresponding silanol 2 was carried out in THF, at room temperature, and under air (Scheme 1). The oxidation reaction required both oxygen and water to evolve, but the oxygen atom incorporated in the produced silanol originated from water as previously demonstrated using ¹⁸O-labeling.¹⁰



Fig. 2. TEM pictures of s-AuCNT (a) and l-AuCNT (b) with respective statistical nanoparticle size analyses (c and d).



Scheme 1. Oxidation of dimethylphenyl silane.

Investigations of the size effect of the supported gold nanoparticles thus started with the oxidation of dimethylphenyl silane using 0.1 mol % loading of s-AuCNT or l-AuCNT. The two reactions were run in parallel under the same conditions, and the time needed to reach completion was assessed. While full oxidation of dimethylphenyl silane required only 45 min of reaction in the case of the s-AuCNT, the same transformation necessitated 150 min using l-AuCNT. It is to be noted that selectivity toward the preferential formation of phenyldimethyl silanol was high as no siloxane by-products could be detected in neither of these experiments. As the observed superior activity of the s-AuCNT presumably originated from increased surface-to-volume ratios and therefore to an increased fraction of exposed gold atoms, further investigations were undertaken by not only taking into account the total gold content of the catalyst but also the gold surface atoms.

To scrutinize the differences between the two hybrids, early kinetics of the reaction was studied using 100-time less catalyst (0.001 mol %) than in the above reaction. Fig. 3 shows the plot of the number of moles of silanol **2** produced per mole of gold as a function of time. For each catalyst, the plot is given either with respect to the total gold content or to the surface atoms only. The turnover frequencies (TOF) of the catalysts can be extrapolated from the slopes of the corresponding early kinetics. The turnover frequency calculated based on the total gold content (TOF_{tot}), was 15,140 h⁻¹ for s-AuCNT, whereas the TOF_{tot} of l-AuCNT was only 2025 h⁻¹. From these values, it appears that, when the overall gold loading is considered, smaller particles (s-AuCNT) are far more active than larger ones (l-AuCNT). However, when focusing on surface atoms, those that are likely to be catalytically active, differences between the two catalysts were far less pronounced. Indeed, turnover values

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