



# Hydrophobic gold catalysts: From synthesis on passivated silica to synthesis on few-layer graphene



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## ABSTRACT

Hydrophobic gold catalysts have recently proven useful in increasing the efficiency of the aerobic oxidation of hydrocarbons in apolar liquid media. Catalytically active 3 nm gold nanoparticles can be dispersed on the surface of commercially available methyl-terminated silica by performing chemical reduction of triphenylphosphine gold(I) chloride in the presence of the support in an ethanol/dichloromethane mixture. This method is here applied to a home-made few-layer graphene which displays a pristine graphitic surface, as shown by thermogravimetric analysis. Since direct application of the protocol leads to much larger gold particles, the protocol of synthesis is subsequently adapted to the specific nature of the graphene support, in particular by performing the reaction under sonication. Further studies of the effect of several reaction parameters on both the average gold crystallite size determined by XRD and the deposition yields determined by elemental analysis reveal (1) the superiority of DMF in minimizing the gold particle size and (2) the impact of short reduction times on maximizing the deposition yields. Repeatability of the experiment is ensured by the development of an optimized protocol of synthesis, and in particular the identification of the most effective positions in the sonication bath.

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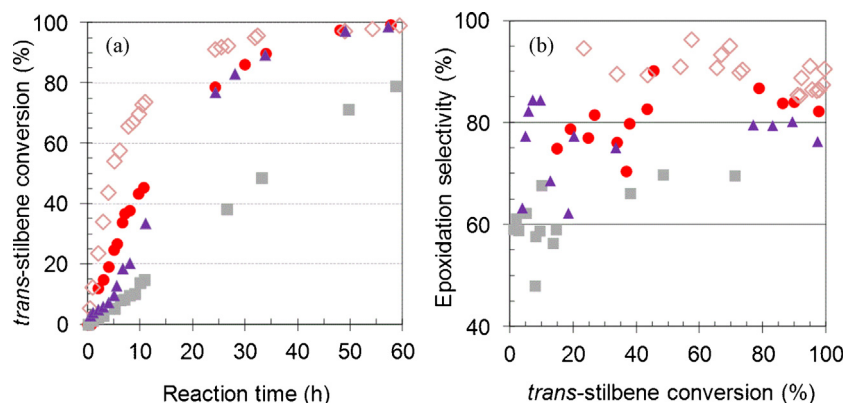
## 1. Introduction

The discovery of the catalytic activity of supported gold nanoparticles (NPs) by Haruta [1] triggered various incentives towards the use of gold as oxidation catalysts from the early nineties. Initially aimed at replacing Pt in a straight forward manner, due to the lower and more stable cost of the raw material, the interest is still intact nowadays despite the dramatic increase in the price of gold, due to the unequalled activity at low temperature of those gold NPs [2]. This low temperature activity in reactions such as the oxidation of CO [3] or the water-gas shift reaction [4] however relies on the use of supports described in the early stages as “active” due to their role in oxygen activation, i.e. titanium oxides and related transition metal oxides [5]. Hence, most methods for the preparation of gold catalysts initially focused on those reducible supports [6,7].

It was later found that alumina-supported gold catalysts could also be active in the oxidation of CO, especially when hydrogen was present in the feed. In addition to preventing deactivation of the catalyst [8] and allowing regeneration of deactivated catalysts [9,10], hydrogen is indeed thought to open up new oxidation pathways [11], by e.g. the in-situ formation of peroxy-type species [12], which are basically independent from the support [13,14]. This triggered a new field of research in which gold NPs did not need to be associated with reducible oxides, as long as the oxidation was carried out in the presence of a sacrificial reductant which ensured oxygen activation. This led to the development of Au/Al<sub>2</sub>O<sub>3</sub> catalysts [15] for the preferential oxidation of CO in the presence of hydrogen (PROX reaction), as well as Au/TS-1 bi-functional systems for the epoxidation of propylene with H<sub>2</sub> and O<sub>2</sub> [16].

Such oxide-supported gold catalysts are generally prepared from reaction between a gold precursor (mostly HAuCl<sub>4</sub>) and the hydroxyl groups present on the support surface [17,18], followed by reduction. Alternative methods in which the gold precursor is first chemically reduced in solution before the resulting sol is adsorbed on the support also lead to efficient catalysts [19–21]. The resulting hydroxyl-terminated gold catalysts are indeed perfectly suited to

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**Fig. 1.** Order of reactivity (a) and selectivity (b) in gold-catalyzed aerobic *trans*-stilbene (ts) epoxidation in methylcyclohexane (MCH) over soluble Au@SiC<sub>8</sub> [36] (◇), a surface-passivated Au<sub>p</sub>/SiO<sub>2</sub> powder [27] (●), nanocrystalline Au/TiO<sub>2</sub>:Gd<sup>3+</sup> [26] (▲) and the Au/TiO<sub>2</sub>-WGC reference gold catalyst for CO oxidation [37] (■). Reaction conditions: tS 1 mmol, MCH 155 mmol, Au 2 μmol, TBHP 50 μmol, 80 °C, 700 rpm, air 1 atm.

gas phase reactions in which those functions can act as promoters [22,23].

However, these oxide-supported gold catalysts turned out to be only poorly dispersed within the aerobic media used for hydrocarbon oxidation in the liquid phase, because the hydrophilic oxide surfaces only have a poor affinity with apolar substrates and solvents [24]. As a result, the reaction rates observed in e.g. the Au/MO<sub>x</sub>-catalyzed *aerobic* co-oxidation of stilbene and methylcyclohexane appear diffusion-limited [25,26]. Besides, hydroxyl groups are known to alter the selectivity of the epoxidation [27]. The performances of the gold-catalyzed aerobic epoxidation of stilbene mediated by methylcyclohexane [28] have been improved over the years by the design of new catalytic materials, with optimized surfaces and affinity for the apolar reaction media (Fig. 1). Recently, a reference catalyst was prepared for this reaction by developing a straightforward method to decorate the surface of a commercially available methyl-terminated silica support with 3 nm gold particles [29]. This method, which is based on the direct chemical reduction of the triphenylphosphine gold(I) chloride complex in an ethanol solution containing a suspension of the hydrophobic powder, can in principle be applied to other supports.

In particular, it appeared interesting to evaluate the potential of this method to disperse gold particles over pristine graphitic surfaces. Indeed, the fully aromatized carbon surface could interact with the triphenylphosphine ligand of the gold complex in  $\pi$ - $\pi$  interactions [30], offering a great number of ordered adsorption sites. It could provide an alternative to the typical methods for metal decoration of carbonaceous surfaces, which generally use oxygenated functions of an oxidized version of the carbon material (e.g. graphite oxide) as adsorption sites [31], such as e.g. “strong electrostatic adsorption” [32] or covalent grafting [33,34]. It is noted that the  $\pi$ - $\pi$  interactions expected between the gold complex and the pristine graphitic surface are anticipated to be much weaker than that engineered by pyrene functions. It is underlined that the aim of the present work is not to firmly immobilize gold complex and carry out heterogenized catalysis [35] but instead, to make use of a soft interaction between the complex and the surface that may allow one to control the growth of the metal particle on the support surface upon reduction.

In this paper, we thus report on the direct chemical reduction of AuPPh<sub>3</sub>Cl in the presence of a home-made few-layer graphene (FLG) and discuss its potential towards dispersing gold NPs over the pristine graphitic surface. In particular, we show how the initial contact time (i.e. time of reaction between the gold precursor and FLG prior to reduction), the reduction time (i.e. time of reaction after the introduction of the chemical reductant) and the solvent

of reaction influence the size of the resulting gold NPs supported on graphene, as well as the gold loading. After observation of lack of reproducibility in the *N,N*-dimethylformamide solvent, we also present the development of an optimized protocol for the synthesis of Au-FLG composites that guarantees repeatability in organic solvents.

## 2. Materials and methods

### 2.1. Synthesis protocols

The synthesis solvents, namely acetonitrile (ACN, 99.99%, ACROS), dichloromethane (DCM,  $\geq 99.8\%$ , Carlo-Erba), *N,N*-dimethylformamide (DMF,  $\geq 99.8\%$ , Sigma-Aldrich), ethanol (EtOH,  $\geq 99.9\%$ , Carlo-Erba), methanol (MeOH,  $\geq 99.9\%$ , Carlo-Erba) and toluene (99.5%, Carlo Erba), are used without further purification.

#### 2.1.1. Few-layer graphene

FLG is synthesized from expanded graphite by surfactant-assisted exfoliation in the liquid phase [38,39], via a typical sonication/sedimentation process using toluene as solvent and Triton X-100 as surfactant. In more details, 3 g of expanded graphite (Mersen, ex-Carbone Lorraine) and 9 g of Triton X-100 (Laboratory grade, Sigma-Aldrich) are placed in a beaker together with 900 mL of toluene. The mixture is then sonicated (Bandelin HD2200 probe sonicator, 30% of 200 W, 20 kHz) in 2 cycles of 30 min, with a 10 min sedimentation step between the 2 cycles. After 10 min sedimentation, 300 mL of the upper part of the partially sedimented mixture is extracted. After filtration, the lighter FLG flakes (i.e. those containing the smallest number of layers) are collected on the filter, while the supernatant is poured back into the beaker. The 900 mL mixture is submitted to two more sonication/sedimentation/extraction/filtration cycles, using the same filter paper on which the FLG is accumulated. The FLG is then washed with 900 mL of ethanol and dried in an oven at 90 °C overnight.

The obtained FLG (typically  $1.6 \pm 0.2$  g) is further treated under flowing argon (ca. 200 mL min<sup>-1</sup>, ramp of 10 °C min<sup>-1</sup> up to 900 °C followed by a 3 h isotherm at 900 °C) in order to remove all residual volatile products and surfactant traces, as set-up in previous work [40].

#### 2.1.2. Au-FLG composites: Decoration of the FLG surface with Au NPs by chemical reduction of AuPPh<sub>3</sub>Cl in the presence of FLG

Prior to each synthesis, fresh solutions of sodium borohydride (10<sup>-2</sup> M) and of the gold precursor (2.5 × 10<sup>-3</sup> M) are prepared by

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