



Design of novel indium oxide supported gold nanocatalysts and their application in homocoupling of arylboronic acids



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ARTICLE INFO

Article history:

Received 16 December 2013

Received in revised form 29 January 2014

Accepted 31 January 2014

Available online 11 February 2014

Keywords:

Au nanoparticles
Biaryls
Catalyst design
Electrolysis
Homocoupling
Indium oxide

ABSTRACT

Gold (Au) nanoparticles stabilized on metal oxide supports offer superior catalytic activity and recyclability in organic catalysis. We report for the first time synthesis of indium oxide stabilized gold (Au@In₂O₃) nanocatalysts using an electrochemical procedure and their application in homocoupling of arylboronic acids. In₂O₃ nanoparticles prepared via sol-gel process are subjected to sacrificial anode electrolysis (SAE) under inert condition for electrodeposition of nano Au on In₂O₃. Thus Au@In₂O₃ nanoparticles obtained are thermally annealed at high temperature to partially oxidize Au and to remove any surfactants. XPS results show the existence of both elemental (nano Au⁰) and cationic (Au³⁺) species in Au@In₂O₃ nanocatalysts, while SEM images confirm the presence of nanoscale Au (<10 nm) particles on In₂O₃ surface. Au@In₂O₃ nanocatalysts are tested for arylboronic acids homocoupling under different conditions and it is found that they are highly active in organic medium with K₂CO₃ base and demonstrate excellent conversion (>97%) and selectivity (>98%). The catalyst recyclability and performance towards differently substituted arylboronic acids is also studied and a plausible mechanism of action is proposed.

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1. Introduction

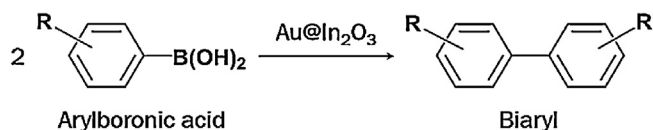
In late 1980s, Haruta et al. [1,2] discovered that nanoscale gold (Au) stabilized on metal oxide supports is catalytically active and can be utilized for CO oxidation at temperatures below 0° C. This fascinating discovery ascended an overwhelming interest in the field of supported Au nanocatalysts and a vast majority of afterwards concentrated on developing new methods for synthesis of supported Au nanoparticles, studying the effect of different oxide supports, applications of supported Au nanocatalysts in environmental and organic catalysis, and investigating the mechanism of action of these supported Au nanocatalysts [3–9]. These studies conclude that catalytic performance of Au nanoparticles stabilized on different oxide supports is determined by the Au particle size, their fine distribution on support surface and stabilization, and the catalyst structure. Therefore, the principal role of metal oxide support is to prevent particle growth and to stabilize Au nanoparticles against coalescence.

The support material, however, may affect the catalytic process directly or indirectly [6]. For this purpose, different types of metal oxides have been exploited as support materials for stabilizing Au nanoparticles. The most frequently used forms of supported Au nanocatalysts are: Au@TiO₂ [10], Au@ZrO₂ [11], Au@Fe₂O₃ [12], Au@Al₂O₃ [13], and Au@CeO₂ [14]. However, indium oxide (In₂O₃) has been scarcely used as a metal oxide support for stabilizing gold nanoparticles, although a few recent examples demonstrate its individual catalytic activity [15–17]. Rodríguez-González et al. [18] reported that Au@In₂O₃–TiO₂ composite catalysts with 6 or 12 wt% In loading were catalytically more active for low-temperature CO oxidation as compared to Au@TiO₂ catalyst. Furthermore, authors claimed that Au@In₂O₃–TiO₂ composite catalysts were more stable than Au@TiO₂, due to a stronger anchoring of nano Au on In₂O₃ and to the structural defects induced by In doping of the anatase TiO₂ support [18].

We therefore selected In₂O₃ as a novel support material for stabilizing Au nanoparticles, and to test the catalytic activity of the Au@In₂O₃ nanocomposite we chose the homocoupling of arylboronic acids (Scheme 1), which is a well known C–C bond forming reaction useful for the preparation of symmetrical biaryls, a class of organic compounds whose skeleton is commonly found in a variety of natural products [19]. Biaryls are also useful building blocks for

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Scheme 1. The homocoupling of arylboronic acids.

synthesis of pharmaceuticals, conducting materials, agrochemicals, supramolecules, and ligands for asymmetric catalysis [20–23].

Earlier, Pd catalyzed homocoupling of arylboronic acids has been studied by some groups [24–27]. Corma et al. [28] first found that Au nanoparticles supported on nanocrystalline CeO₂ (Au@CeO₂) exhibit high catalytic activity and selectivity in the coupling reaction of arylboronic acids. Willis and Guzman [29] studied both the influence of various oxide supports (SiO₂, TiO₂, ZrO₂, and CeO₂) on stabilization of Au nanoparticles (~10 nm) and activity of the obtained catalysts on the same process. They found that all supported Au nanocatalysts except Au@SiO₂ show good selectivity towards biaryls.

It is believed that the preparation procedure also plays an important role in determining the Au nanocomposite properties, such as sizes, morphology, dispersion, and catalytic activity. Albeit different protocols have been reported in literature, the *adsorption* and *deposition-precipitation* procedures are the most general and widely recognized methods [3,6,8]. However, we employed a different approach for preparing Au@In₂O₃ nanocatalysts deriving from the well-established *sacrificial anode electrolysis* (SAE) procedure, first developed by Reetz and co-workers for the synthesis of nanostructured metal clusters [30,31]. This method is very effective for preparing core-shell Au nanoclusters with narrow size distribution [30–32].

Hereby, we report a slightly modified SAE procedure for electrolytic deposition of nanoscale Au on In₂O₃ nanoparticles, obtained via pH controlled sol-gel process. After electrolytic deposition, Au@In₂O₃ nanocatalysts were thermally annealed to remove surfactants, to partially oxidize Au (being the gold cationic species important for catalysis [28]), and for appropriate affixing of Au on In₂O₃ supports. Thus Au@In₂O₃ obtained nanocatalysts are found to be stable and highly active towards selective homocoupling of substituted arylboronic acids in organic solvents and ionic liquids.

2. Experimental

All chemicals and reagents are obtained from Sigma-Aldrich in the highest available purity and are used as received without further purification except tetraoctylammonium chloride (TOAC) that is vacuum dried for 4 h before use in order to remove traces of water. High purity gold and platinum foils (size: 25 × 25 mm; thickness: 0.25 mm; purity: 99.999%) are purchased from Goodfellow, which are used as the anode and the cathode respectively during the electrolysis process. Both the electrodes are properly cleaned with alumina powder, acetone, deionized water and acetone respectively and they are dried (stored) in nitrogen (N₂) before use.

2.1. Procedure for synthesis of In₂O₃ support nanoparticles

Indium oxide (In₂O₃) support nanoparticles are prepared via pH controlled aqueous sol-gel process. A solution of InCl₃ (0.1 M, 100 mL) is prepared in double distilled, deionized water and is warmed at 70 °C for 1 h. Afterwards, liquid ammonia solution (0.1 M NH₄OH) is added drop-wise to InCl₃ solution to attain a pH of 9. At pH = 9, the mixture is aged for another hour at 70 °C with continuous stirring and white precipitates are obtained via centrifuge. The precipitates are washed with excess deionized water to remove

any unreacted species (ions) and traces of ammonia, and are subsequently dried in an oven at 120 °C for 2 h to get In₂O₃ powder. Thus In₂O₃ obtained powders are characterized by XPS and SEM to study surface chemical structure and morphology, respectively.

2.2. Procedure for synthesis of Au@In₂O₃ nanocatalysts

Au@In₂O₃ nanocatalysts are prepared via sacrificial anode electrolysis procedure carried out in an air tight, three-electrode cell equipped with an Au anode, a Pt cathode, an Ag/AgNO₃ (0.1 M in ACN) reference electrode, and nitrogen (N₂) gas inlet and outlet. The area of solid electrodes is about 1.25 cm². The electrodes are immersed in the electrolyte solution (0.05 M, 5 mL) composed by vacuum dried TOAC in anhydrous tetrahydrofuran (THF) and acetonitrile (ACN) mixed in 3:1 ratio. TOAC acts as the supporting electrolyte as well as the surfactant for partial stabilization of Au nanoparticles. In₂O₃ support particles (100 mg) are also added to the electrolytic cell and the mixture is stirred to yield a homogeneous suspension of In₂O₃. The electrolysis is performed in the potentiostatic mode under continuous supply of N₂, and the process is stopped after the total charge reached 100 C. The working electrode potential is fixed at +1.5 V against the reference electrode during the electrolysis [31]. A schematic of the SAE procedure is shown in Fig. 1. The as-prepared Au@In₂O₃ nanocatalysts are characterized by XPS and SEM to study surface chemical speciation, nature of Au, and surface morphology.

2.3. Thermal treatment of Au@In₂O₃ nanocatalysts

The as-prepared Au@In₂O₃ nanocatalysts are centrifuged at 6000 rpm to separate colloidal core-shell Au nanoparticles from Au@In₂O₃ nanocatalysts. After separation, the heavier Au@In₂O₃ are thermally annealed at 750 °C for 2 h in air (O₂ atmosphere) to remove surfactant from the nanoparticles surface, partially oxidize Au, properly affix Au nanoparticles on In₂O₃ supports, and investigate the influence of thermal treatment on the structure, morphology and stability of Au@In₂O₃ nanocatalysts. Finally, the nanocomposite is also characterized by XPS and SEM techniques, as mentioned below.

2.4. XPS characterization of Au@In₂O₃ nanocatalysts

The surface analyses of In₂O₃ nanoparticles and Au@In₂O₃ nanocatalysts before and after thermal treatment are obtained with the help of an X-ray photoelectron Thermo VG Theta Probe spectrometer equipped with a micro-spot monochromatized Al K α source. Both survey scans and high resolution spectra are acquired infixed analyzer transmission mode with pass energy of 150 and 100 eV, respectively. For this purpose, a thick film of the respective nanoparticle suspensions is coated on a platinum substrate, which prevents the onset of differential charging surface phenomenon and resulting alteration in the photoelectron peak shape and FWHM. The XPS data are processed with the *Avantage* software [33]. The aliphatic C1s component fixed at BE values of 284.8 ± 0.1 eV is referenced for calibration of the binding energy (BE) scale. The surface chemical speciation (in at%) of each sample is determined by evaluating the integrated peak areas of the principle photoelectron peaks and the respective sensitivity factors, as described elsewhere [34].

2.5. SEM characterization of Au@In₂O₃ nanocatalysts

The morphology of In₂O₃, Au nanoparticles, and Au@In₂O₃ nanocatalysts before and after thermal treatment is ascertained by field emission scanning electron microscope (FE-SEM), mod.

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