



Thermally reduced gold nanocatalysts prepared by the carbonization of ordered mesoporous carbon as a heterogeneous catalyst for the selective reduction of aromatic nitro compounds



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ARTICLE INFO

Article history:

Received 5 August 2016

Revised 18 September 2016

Accepted 20 September 2016

Available online 31 October 2016

Keywords:

Gold nanoparticles

Thermal reduction

Surface modification

Ordered mesoporous carbon

Selective hydrogenation

ABSTRACT

In this study, we propose gold-intercalated ordered mesoporous carbon nanosphere catalysts in which gold nanoparticles are reduced by high-temperature carbonization of the carbonaceous matrix to catalyze the selective hydrogenation of aromatic nitro compounds. A spherical morphology of particles with size approximately 90 nm and ordered mesoporous arrays was clearly observed on the surface in the high-resolution scanning electron microscopy images. The X-ray photoelectron spectra and transmission electron microscopy images showed that the dispersed metallic gold nanoparticles (2.8 nm in diameter) were intercalated into a carbon framework. The IR spectra for CO chemisorption suggested the involvement of neutral gold atoms in a low-coordination state in clusters or a stepped surface. The gold nanocatalysts intercalated into the nanospherical mesoporous carbons exhibited high activity and selectivity for the hydrogenation of nitroarenes to the corresponding amines, using H₂ as a reduction agent. The initial reaction rate reached 12.7 and 6.5 min⁻¹ in the hydrogenation of *p*-chloronitrobenzene and 4-nitrophenol, respectively. This catalytic performance was retained for more than five catalytic runs with no obvious activity loss or gold leaching, indicative of high stability. The trapping test using a mercapto-functionalized SBA-15 solid revealed undetected soluble gold species in the reaction solution. The high activity and stability of the ordered mesoporous carbon nanosphere-supported gold catalysts was strongly correlated to the particle morphology change by thermal reduction, which can generate new low-coordinated gold atoms for intercalated gold NPs in the matrix.

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1. Introduction

Gold nanocatalysts represent a new generation of catalysts for the reduction of nitroarenes to aminoarenes using H₂ or NaBH₄ [1–3]. Such nanocatalysts exhibit substantially better selectivity and stability than platinum-group metals [4–6]. Oxide supports such as CeO₂, TiO₂, Fe₂O₃, and Al₂O₃ are typically used to isolate small metal nanoparticles with a narrow size distribution [7–9]. For example, Corma et al. reported a Au/TiO₂ catalyst that is highly efficient for the selective reduction of nitro moieties with various functional groups by H₂ [1]. The rate-determining step was H₂ dissociation on the Au surface [10]. Density functional theory (DFT) calculations have revealed that the stronger Au–H interaction at the low-coordinated corner sites of the gold surface or at the edge or corner atoms of the gold nanoparticles can lead to a lower H₂

dissociation barrier [11]. Therefore, the support strongly influences the number of potentially active sites for H₂ dissociation, which depends on the particle shape. In the case of titania, low-coordinated neutral gold atoms have been demonstrated to be the active sites on which H₂ can be adsorbed and dissociated [12]. Neither the atoms directly bonding to oxygen nor those in contact with the oxide in the first atom layer are relevant to the activity toward the dissociation of H₂. The O vacancy defects on the TiO₂ surface preferentially stabilize the active isomers. The catalytic activity is then enhanced. In contrast, globally positively charged Au particles supported on the stoichiometric TiO₂ surface and negatively charged gold over the reduced surface do not affect the H₂ dissociation activity [12].

Ordered mesoporous carbons have many advantages over oxides as substrates, including tailorable porosity, surface chemistry, electron conductivity, and stability [13–15]. The interaction between the activated carbon and gold is distinctly weak. The intrinsic nature of the gold surface could be investigated directly.

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However, compared with the methods developed for preparing oxide-supported nanocatalysts, those available for preparing gold-containing mesoporous carbon materials are limited [16,17]. The sol-gel method can be used to load gold onto porous carbon [18–20]. The protecting agent for the gold sols may influence the overall activity of the gold nanocatalysts in several ways, including influencing the nanoparticle size [21], steric hindrance, and electronic properties [7]. Particles grow during the calcination of the protecting agent, and a sharp decrease in the catalytic activity can occur [22]. Another serious problem that can substantially reduce the activity is the detachment of nanoparticles when the carbon support is reused [23].

Our group has reported an evaporation-induced self-assembly (EISA) method for the synthesis of intercalated gold nanoparticles inside carbonaceous walls [24]; however, the nanoparticle size is approximately 9 nm. An extra precarbonization step involving refluxing in sulfuric acid can reduce the particle size, but this additional step is time- and energy-consuming. In addition, the nature of the surface of the thermally reduced gold nanoparticles is unclear. In fact, the literature contains few reports focused on the nature of the surface of intercalated nanoparticles in activated carbon, possibly because of the diverse origins of carbon. Ru nanocatalysts embedded inside carbon or carbon-coated silica pore walls exhibit enhanced activity toward toluene hydrogenation because of contact between the metallic particles and carbonaceous carriers on the interface [25]. We have previously synthesized transition-metal oxides (e.g., MnO and TiO₂) intercalated into ordered mesoporous carbon [26–28]. Doping elemental C into the MnO or TiO₂ lattice possibly provides Mn–C or Ti–O–C bonds, modifies the surface energy of the transition metal oxide, and results in the expression of surfaces with different structures. Coordinatively unsaturated MnO is formed, which exhibits high activity toward the oxidation of phenol [26]. These phenomena stimulate our research interest in the nature of the surface of intercalated gold nanoparticles inside mesoporous carbon, which has rarely been reported.

Here, for the first time, we report a hydrothermal synthesis method for the intercalation of dispersed gold nanoparticles (approximately 2.8 nm in size) inside ordered mesoporous carbon nanospheres (approximately 90 nm in diameter). The simultaneous thermal reduction of gold nanoparticles and carbonization of the matrix facilitates the involvement of gold inside the carbon matrix, the formation of clusterlike structures by the diffusion of carbon atoms into the gold, and the change in particle morphology induced by CO adsorption. Aggregation and leaching are inhibited either at a high temperature of 700 °C or after repeatable catalytic reactions, which are serious in gold-supported activated carbon catalysts. The morphology of the nanoparticles, which can generate new low-coordinated gold atoms, can greatly improve the catalytic performance of gold nanocatalysts in the hydrogenation of aromatic nitro compounds.

2. Experimental

2.1. Preparation of ordered mesoporous carbon nanosphere-supported gold catalysts

In a typical synthesis of ordered mesoporous carbon nanosphere-supported gold catalysts (Au/MCN), a mixture containing phenol (0.6 g), a formalin aqueous solution (37 wt.%, 2.1 mL), and NaOH (0.1 M, 15 mL) aqueous solution was heated to 70 °C under stirring. After 30 min, a clear solution composed of 1.2 g of Pluronic F127 (*M*_w = 12,600, PEO₁₀₆PPO₇₀PEO₁₀₆, Acros Corp.) and 15.0 g of deionized water was added. The temperature was then adjusted to 66 °C. The mixture was stirred at

340 ± 40 rpm for 3 h. A solution that was premade by mixing 0.128 g of 3-mercaptopropyltrimethoxysilane (MPTMS, minimum 98 wt.%, Acros Chemical Inc.), 1.5 mL of HAuCl₄ aqueous solution (24.3 mmol L⁻¹), and 50 g of deionized water was added. Deposition occurred after approximately 16–18 h, and the reaction was immediately terminated. After quiescence, until the deposits were dissolved, deionized water was added to dilute the solution (56 mL of H₂O added to 17.7 mL of the obtained solution). The solution was then transferred into several autoclaves and heated at 130 °C for 1 day, after which the autoclaves were rapidly cooled to room temperature. After the products were separated, washed with deionized water several times, and dried, approximately 1.4 g of a yellow solid was obtained. The yellow solid was calcined at 700 °C for 2 h under high-purity N₂ to eliminate the triblock copolymer templates and carbonized resins. A black product (0.78 g) was obtained. By tuning the HAuCl₄ amount to 0.75 mL while maintaining the other parameters and processes of a typical synthesis, we obtained a gold catalyst with varied metal content; this product is denoted by 0.5Au/MCN.

For comparison, a sample beginning with resol and HAuCl₄ was prepared in the absence of the silane coupling agent while all other procedures were kept constant; this product is referred to as Au/C. Gold particles protected by citrate were obtained according to a well-established procedure. Commercially activated carbon-supported gold catalysts (Au/AC(DR)) with a gold loading of 0.89 wt.% and Au/TiO₂ with a gold loading of 0.96 wt.% were purchased from Harura Gold Inc. (Japan). The Au/AC(DR) catalyst was synthesized by the deposition–reduction route [29], which avoids the use of a polymer protecting agent. The detailed synthesis procedure and characterization results for these reference samples are provided in the [Supplementary Material \(Figs. S1–S5\)](#).

2.2. Selective reduction of aromatic nitro compounds

The liquid-phase hydrogenation of aromatic nitro compounds was carried out in a commercial stainless steel reactor (25 cm³ autoclave, Parr, USA) equipped with a pressure-controlled H₂ supply system. *p*-Chloronitrobenzene (*p*-CNB) (0.32 mmol) or 0.36 mmol of 4-nitrophenol (4-NP) and 5 mL of ethanol with 10.0 mg of the solid catalyst Au/MCN (10.4 mg for Au/TiO₂) were mixed with 4-NP/Au and *p*-CNB/Au at molar ratios of 706 and 623, respectively. The reactor was flushed seven times with 0.8 MPa of H₂ before it was pressurized to the desired H₂ pressure of 4.0 MPa and placed in an oil bath that was maintained at 140 °C. The stirring rate was maintained at 600 rpm. The reaction was quenched at various reaction times by immediately cooling the autoclave. The reactor was washed using 5 mL of ethanol, and the total solvent amount was 10 mL. The solid catalyst was separated and extracted using 5 mL of ethanol. The extract and filtrate were characterized by gas chromatography (Agilent Technologies 7890B) using a DB-1 column and a flame ionization detector (FID). Each test was repeated at least three times, and the experimental errors were within ±5%. The carbon balance was maintained at a 5% difference. The catalytic results are shown as the conversion of 4-NP or *p*-CNB, the selectivity of 4-aminophenol (4-AP) or *p*-chloroaniline (*p*-CAN), an initial rate (*r*₀, mmol of reacted reactant per mmol of Au and minute of the initial reaction period), and the turnover number (TON, total converted nitroarenes on the basis of total gold atoms). The hydrogenation was repeated three times with the same initial rates, and the total reaction times were within ±8%.

The recycling tests were performed under the aforementioned reaction conditions, except for the use of the recovered catalyst. The Au/MCN catalyst was recovered after a completed reaction by being thoroughly washed with ethanol and water, dried under a vacuum at 80 °C and weighed. Several parallel reactions were

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