L-serine-functionalized montmorillonite decorated with Au nanoparticles: A new highly efficient catalyst for the reduction of 4-nitrophenol

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ABSTRACT

The conversion of nitroarenes to aminoarenes is of great industrial interest since they are prevalent pollutants in water and aminoarenes are important intermediates in the synthesis of pharmaceuticals, natural products and in bulk chemical production. In this work, two new catalysts for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) were prepared by immobilization of gold nanoparticles onto the surface of K10 montmorillonite clay (K10) functionalized with two new L-serine derivative organosilanes. Transmission electron microscopy showed the presence of 4–5 nm gold nanoparticles after catalysis. The reduction reaction of 4-NP to 4-AP at 25 °C, using $NaBH_4$ as reducing agent, led to nearly 100% conversion in only 1 minute, presenting pseudo-first-order rate constants normalized for Au loading of $K = 630$ and $430 \ mmol^{-1} \ s^{-1}$. The catalysts showed high stability, leading to substrate conversions of 95–100% after 10 consecutive cycles, with negligible Au leaching.
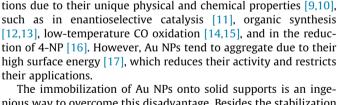
1. Introduction

Generally, nitroarene compounds such as 4-nitrophenol are the most prevalent pollutants detected in water. They are originated from agricultural and industrial sources [1,2]. The conversion of nitroarene to aminoarene compounds is of great industrial importance, since the latter are an important class of compounds used as intermediates in the synthesis of numerous pharmaceuticals, dyes, polymers and natural products [1,3,4] as well as for bulk chemical production.

The reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by sodium borohydride was found by Pal et al. [5] in 2002 using silver nanoparticles as catalyst and, since then, it has become the model reaction to test the catalytic performance of catalysts in aqueous solution [6].

Nanosized metal particles have been a topic of great interest and continue to attract immense attention due to their fantastic physical, chemical and biological properties which lead to potential catalytic applications [7,8]. Among them, Au nanoparticles (NPs) have received a great interest in a wide variety of applica-

tions due to their unique physical and chemical properties [9,10], such as in enantioselective catalysis [11], organic synthesis [12,13], low-temperature CO oxidation [14,15], and in the reduction of 4-NP [16]. However, Au NPs tend to aggregate due to their high surface energy [17], which reduces their activity and restricts their applications.

The immobilization of Au NPs onto solid supports is an ingenious way to overcome this disadvantage. Besides the stabilization improvement by preventing Au NPs agglomeration, this procedure facilitates the recycling of the catalyst. In literature, several reports highlight that Au NPs immobilized onto solid supports, such as graphene oxide [18], titanium dioxide [19] or carbon [20], metal-organic frameworks [21], cerium oxide [22], silica nanoparticles [23], carbon nanotubes [24], ordered mesoporous carbon nanospheres [25] and clays [26], often show enhanced catalytic activity in comparison to free Au NPs. This is due to the strong synergistic interaction that occurs at the interface of the two components [27]. Clays are of particular interest since they are cheap, environmentally-friendly, readily available and have important tunable properties such as high porosity and easy surface modification. Nevertheless, the direct immobilization of the active metal species onto clays usually leads to significant leaching during the catalytic reaction [28,29]. Hence, the functionalization of the inor-

ganic support *via* covalent attachment of suitable organic ligands to which the transition metals will coordinate – thus forming the catalytic complex – is one of the best solutions [30].

Recently, we turned our attention to the study of the potential use of ʟ-serine derivatives as ligands for metal complex formation [31]. Serine has two major advantages for this purpose: it is cheap and easily available and has three functional groups that may be easily functionalized, thus allowing chemical and structural design.

In this work, we report the preparation and catalytic performance of two novel gold-based heterogeneous catalysts in the reduction of 4-NP to 4-AP in an aqueous medium in the presence of $NaBH_4$ reducing agent. The catalysts were prepared by functionalization of K10 montmorillonite clay (K10) with two ʟ-serines presenting different modifications, followed by the immobilization of gold NPs onto its surface. The influence of the type of ʟ-serine on the amount of Au NPs grafted to the support surface and on the catalytic performance was assessed. This work promotes the advance of the design of new gold-based heterogeneous catalysts with high catalytic performance and stability in the reduction of 4-NP.

2. Experimental section

2.1. Chemicals, reagents and solvents

Commercial ʟ-serine **1** (Fmoc-Ser-OH) was purchased from Fluorochem. Sodium borohydride (98%), anhydrous sodium sulfate (≥99%), 4-aminophenol (4-AP, ≥98%), potassium carbonate (≥99%), citric acid (≥ 99.5%), *N,N*-diisopropylethylamine (DIPEA, ≥98%), benzylamine (≥98%), K10 montmorillonite clay, *o*-(benzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium tetrafluoroborate (TBTU, 97%), piperidine (99%), dibutyltin dilaurate (95%) and anhydrous toluene were purchased from Sigma-Aldrich. 3-(triethylsilyl)propyl isocyanate (IsoTES, 95%) was purchased from ABCR. 2-propanol (analytical grade) was acquired from Analar Normapur. Tetrachloroauric(III) acid trihydrate (≥49.0% Au basis) was purchased from Alfa Aesar and 4-nitrophenol (4-NP, analytical grade) from Fluka. The solvents methanol, acetonitrile, ethyl acetate, N,N-dimethylformamide and dichloromethane were purchased from Fisher Scientific. All chemicals were used as received without further purification. Milli-Q ultrapure water (18 MΩ cm) was used in all experiments.

2.2. Materials preparation

2.2.1. Preparation of ʟ-serine derivative organosilanes

The chemical structures of the ʟ-serine derivative organosilanes **4** and **5**, as well as the synthetic pathways used for their preparation are represented in Scheme 1.

The procedures used are described as follows:

(S)-methyl-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-hydroxypropanoate (**2**): 0.1 g of an acidic resin (Dowex 50W-X2) was suspended in a solution of **1** (1.00 g, 3.05 mmol) in dry methanol (20 mL). The mixture was refluxed overnight under stirring and inert atmosphere. The reaction mixture was filtered and the volatiles evaporated at reduced pressure. The solid residue was purified by chromatographic column (eluent: AcOEt). A white solid was obtained with 92% yield.

(S)-(9H-fluoren-9-yl)methyl (1-(benzylamino)-3-hydroxy-1-oxopropan-2-yl)carbamate (**3**): To a solution of **1** (1.00 g, 3.05 mmol) in anhydrous dichloromethane (50 mL) was added TBTU (0.98 g, 3.1 mmol), DIPEA (0.52 mL, 3.1 mmol) and benzylamine (0.34 mL, 3.1 mmol). The solution was stirred under inert atmosphere at room temperature during 2 h (the reaction mixture tends to form a gelatinous crude due to the very low solubility of the product;

hence, the amount of solvent should be enough to avoid gelatinization and the consequent poor reaction homogenization). The solvent was evaporated and the residue was dissolved in hot AcOEt (50 mL). Hot water was added (50 mL), the aqueous phase was separated and the organic phase was washed twice with hot water (50 mL) and brine. The aqueous phase was extracted again with hot AcOEt (50 mL) and the organic layers were gathered and dried over anhydrous Na_2SO_4. The solvent was evaporated at reduced pressure and the gelatinous residue was further purified by recrystallization in AcOEt. After complete dryness over reduced pressure, a white solid was obtained with 85% yield.

Organosilylation of clays: The silylation of ʟ-serines **2** and **3** was performed by following our previously described protocol [32,33]. To a solution of serine **2/3** in anhydrous acetone, 1 eq. of 3-(triethylsilyl)propyl isocyanate and a catalytic amount of dibutyltin dilaurate (DBTDL) were added. The solution was heated up to 120 °C under microwave irradiation (MW) in a closed vessel (CEM 908010 from CEM Discover) until no further evolution of the reaction was verified (monitored by thin-layer chromatography). After cooling, a polystyrene-NH_2 resin was added to the solution, followed by stirring overnight. The resin was filtered off and the solution was evaporated under reduced pressure. Electrospray ionization mass spectrometry (ESI-MS) analysis of the reaction mixture confirmed the formation of the desired products **4** and **5**.

The crude compounds **4/5** were immediately dissolved in anhydrous toluene (50 mL) and a previously dried (12 h at 100 °C) amount of K10 was added (0.8 g mixture/0.8 g K10). The mixture was refluxed for 20 h under inert atmosphere. The resulting materials were washed by reflux in dry toluene during 2 h, filtered and finally dried at 100 °C for 24 h. The functionalized materials will be denoted as K10_**4** and K10_**5**, where the number identifies the ʟ-serine derivative organosilane grafted onto K10. The K10_**4** and K10_**5** materials were submitted to the ninhydrin test, which gave negative results to the presence of free amine groups (Fig. S1 in the Supporting Information). This test also confirmed the efficiency on the elimination of the unreacted IsoTES by the polystyrene-NH_2 resin, since the isocyanate groups also provided a positive result due to their transformation into amine groups during the test procedure.

Deprotection of the amine group: 1 g of K10_**4** was suspended in DMF (10 mL) and 2 mL of piperidine were added. The reaction was left to react at room temperature for 2 h. The material was filtered, washed with dichloromethane and acetonitrile and dried at 80 °C overnight. The material was submitted to a new ninhydrin test, which gave positive result to the presence of free amine groups (dark blue color, see Fig. S1 in the Supporting Information), thus confirming the formation of the material denoted as K10_**A**. A similar procedure was used in order to convert material K10_**5** into material K10_**B**.

2.2.2. Immobilization of Au NPs onto ʟ-serine-functionalized K10

Typically, the K10_**A** or K10_**B** material (500 mg) was dispersed in 300 mL of 2-propanol by sonication. Then, 160 mg of $HAuCl_4.3-H_2O$ (0.05 mmol) and 170 mg of citric acid (0.09 mmol), both separately dissolved in 2-propanol (100 mL), were added dropwise and simultaneously to the functionalized clay dispersion under vigorous stirring. The resulting mixture was kept under vigorous stirring and at room temperature during 2 h. The materials were recovered by filtration through a membrane (Whatman, 0.2 μm) and washed once with 2-propanol (200 mL). The materials will be denoted as K10_**A**@Au and K10_**B**@Au.

2.3. Physicochemical characterization

Liquid-state nuclear magnetic resonance (NMR) analyses were performed at Centro de Materiais da Universidade do Porto