



Selective oxidation of cyclohexene through gold functionalized silica monolith microreactors



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ABSTRACT

Two simple, reproducible methods of preparing evenly distributed Au nanoparticle containing mesoporous silica monoliths are investigated. These Au nanoparticle containing monoliths are subsequently investigated as flow reactors for the selective oxidation of cyclohexene. In the first strategy, the silica monolith was directly impregnated with Au nanoparticles during the formation of the monolith. The second approach was to pre-functionalize the monolith with thiol groups tethered within the silica mesostructure. These can act as evenly distributed anchors for the Au nanoparticles to be incorporated by flowing a Au nanoparticle solution through the thiol functionalized monolith. Both methods led to successfully achieving even distribution of Au nanoparticles along the length of the monolith as demonstrated by ICP-OES. However, the impregnation method led to strong agglomeration of the Au nanoparticles during subsequent heating steps while the thiol anchoring procedure maintained the nanoparticles in the range of 6.8 ± 1.4 nm. Both Au nanoparticle containing monoliths as well as samples with no Au incorporated were tested for the selective oxidation of cyclohexene under constant flow at 30 °C. The Au free materials were found to be catalytically inactive with Au being the minimum necessary requirement for the reaction to proceed. The impregnated Au-containing monolith was found to be less active than the thiol functionalized Au-containing material, attributable to the low metal surface area of the Au nanoparticles. The reaction on the thiol functionalized Au-containing monolith was found to depend strongly on the type of oxidant used: tert-butyl hydroperoxide (TBHP) was more active than H₂O₂, likely due to the thiol induced hydrophobicity in the monolith.

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1. Introduction

The catalytic properties and surface chemistry of Au have been the focus of intense research over the past two decades [1,2]. Gold nanoparticles have been identified as catalytically active for a number of diverse reactions including low temperature CO oxidation [3], selective oxidation reactions [4], hydrogen peroxide formation from O₂ and H₂ [5], coupling reactions [6,7] and hydrogenations [8]. Selective oxidation reactions are of prime economic importance in a diverse range of applications from the production of fine chemicals and synthetic fibres to polymers and paints.

Continuous-flow catalytic microreactors have long been envisaged as a practical, economic and environmentally friendly method of carrying out reactions of importance for a variety of industries including fine chemicals [9,10]. Microreactors present many key advantages over the

traditionally used batch reactors [9]. Such advantages include continuous flow operation, ease of separation of the catalyst from reactants and products as well as the ease of sampling without contamination when removing an aliquot. Of particular importance is the ability to obtain accurate and reproducible control over the reaction conditions such as temperature, pressure and reaction solvent [9,11]. Furthermore, monolithic devices (microreactors containing a porous network of typically silica or other oxide materials) can be functionalized extensively with enzymes [12], magnetic nanoparticles [11] and other functional groups [12–14] in order to tailor their catalytic properties such as selectivity and activity [10,15]. The incorporation of metal nanoparticles in monolithic structures in particular has received attention for its applications in, chromatography [15,16], metal adsorption for contaminant purification [17], C–C coupling reactions [18], reduction of nitrophenols [19] and CO oxidation reactions [20]. In the case of oxidation it has been reported that silica monoliths loaded with either Pt or Pd nanoparticles presented conversions 2.5 times higher in microreactor than when using powder catalysts. This shows that using microreactor technology for selective oxidation reactions enhances the catalytic ability of precious metal catalysts [20]. A major challenge in all cases however is to evenly

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functionalize the catalytically active species along the length of the monolithic microreactor, which is key to maximizing efficient reaction control.

Here we have used a simple reproducible method to synthesise mesoporous silica monolithic reactors and investigated two strategies for evenly functionalizing them with gold nanoparticles along their length. In this way we are aiming to combine (i) a continuous flow monolithic system, which offers a variety of operational and economic benefits with (ii) the unique catalytic properties of Au in selective oxidation catalysis. Two different methods were used to achieve even Au nanoparticle distribution within the monoliths. Firstly, simple impregnation of Au nanoparticles into the monolith during the monolith's formation ensures even/random positioning of the nanoparticles as a result of solution phase mixing. Secondly, tethering thiol groups into the mesoporous structure of the monolith using 3-(mercaptopropyl)trimethoxysilane allows the sulphur groups to act as anchors for the Au nanoparticles which can then be passed through the monolith and be tethered to the thiol groups. As the small thiol groups can diffuse readily through the monolith and react with surface hydroxyls to produce an even coverage, this allows Au nanoparticles to be flowed through the reactor until some saturation coverage of the thiols is reached. At this point the even distribution of the thiol groups confers a similarly even distribution within the monolith upon the anchored gold nanoparticles. As will be shown, both methods do succeed in distributing the gold evenly along the length of the reactor. However, in the case of the impregnated method heat treatment during synthesis, results in heavily agglomerated Au nanoparticles. In contrast, the material containing thiol groups that can act as anchoring sites for the Au nanoparticles led to a material that was not only evenly dispersed along the length of the monolith but also exhibits a smaller particle size and more uniform particle size distribution.

The materials synthesised were tested for the selective oxidation of cyclohexene [21]. The reason behind the choice of cyclohexene as the test molecule is the volume of data that exists in the literature, which allows for the appropriate choice of reaction conditions [22]. The oxidation of cyclohexene has been utilised as a model reaction in selective oxidation studies [23–25]. Two common liquid phase oxidants were employed: hydrogen peroxide (H_2O_2) and tert-butyl hydroperoxide (TBHP) [22,26,27]. The Au free monoliths were found to be catalytically inert at 30 °C. The presence of Au was the minimum necessary requirement for the selective oxidation reaction to proceed. Both Au functionalized monoliths were found to be active for the selective oxidation of cyclohexene (Fig. 1) with the thiol functionalized monolith being more active as compared to the impregnated monolith due to the better dispersity and higher surface area of Au. The oxidation reaction on the Au–thiol functionalized monolith was found to depend on the type of oxidant used with TBHP being more active than H_2O_2 . We

suggest this can be attributed to the thiol modifier (containing propyl groups) rendering the silica surface of the monolith more hydrophobic than the hydroxyl termination of the bare silica surface and so favouring the organic oxidant.

2. Experimental

2.1. Materials synthesis

2.1.1. Au nanoparticle synthesis

Au nanoparticles were prepared by adapting the synthetic method described by Liu et al. [28] $H AuCl_4 \cdot 3H_2O$ (24 mg) (Alfa Aesar, 99.99% purity) was dissolved in ethylene glycol (1 mL, Fisher Scientific > 99%). To the solution, polyvinylpyrrolidone (22 mg, MW 40,000, Alfa Aesar) was added followed by a further 6 mL of ethylene glycol and mixed for 10 min. Sodium borohydride (30 mg) was then added to the mixture and heated at 80 °C under N_2 for 30 min. The nanoparticles were isolated by the addition of acetone followed by centrifugation at 3500 rpm. This process was repeated three times. The nanoparticles were then dispersed in deionised water. The method was found to produce Au nanoparticles of 2.5 ± 0.7 nm size, as shown in the supporting information (Fig. S1).

2.1.2. Silica monolith synthesis

The monolith design was based upon existing designs and dimensions to ensure good thermal control [11,29]. Mesoporous silica monoliths were prepared by a modification of the method established by Fletcher et al. [11,29]. Poly(ethylene oxide) (MW 200,000, 0.122 g, Sigma Aldrich) was added to a solution of acetic acid (0.02 M, 1.6 mL, Aldrich, purity 97.9%) and stirred for 1 h (with a magnetic stirrer at 200 rpm) in an ice bath until fully homogeneous. Tetramethylorthosilicate (TMOS) (800 μ L, Sigma Aldrich, purity 98%) was added to the solution over a period of 1 h until once again homogeneous. The solution was subsequently poured into a plastic mould (length 6 cm, internal diameter 0.45 cm), closed at both ends using poly(tetrafluoroethylene) (PTFE) thread seal tape. This was then aged at 40 °C for 3 days. The gel monolith was removed from the mould and washed thoroughly with deionised water to remove any trace residues. The monolith was then immersed in an incubator containing ammonium hydroxide solution (1 M). The solution was heated to ~ 82 °C for 24 h, to form a mesoporous network within the material. This was followed by further washing with deionised water to remove residual ammonium hydroxide until pH 7 was achieved. The monolith was dried at 40 °C for 1 day. The clean and dry monolith rods were heated at 600 °C for 3 h under air flow to remove the remaining poly(ethylene oxide). The rod was then cut to a 4 cm length, and linked to a borosilicate tube (Smith Scientific) via a PTFE heat shrinkable tube. This was heated in an oven at 350 °C for 1 h to seal the tube and encapsulate the monolithic rod.

2.1.3. Au nanoparticle impregnated silica monolith synthesis

Au nanoparticle impregnated silica monoliths were prepared as described above, however after addition of the tetramethylorthosilicate, one hour after this was homogeneously mixed, the Au nanoparticle suspension in water was also added (0.4 M, 150 μ L). The resulting mixture was then mixed until homogenous (0.5 h). The synthesis was then completed following the same process described above for the Au free monolith.

2.1.4. Au–thiol functionalized silica monolith

Once synthesised, a mesoporous silica monolith can be functionalized by incorporating a variety of useful functional groups such as: vinyl-, allyl-, amino-propyl and sulphur [12,30]. Functionalizing the silica monolith with these examples offers additional binding sites for ligands (vinyl-, allyl- and amino-propyl) that require a specific environment. In the present case thiolation of the monolith was performed to anchor Au nanoparticles. As the Au–S bond is relatively strong and the thiolate ligand is also reasonably durable on the silica

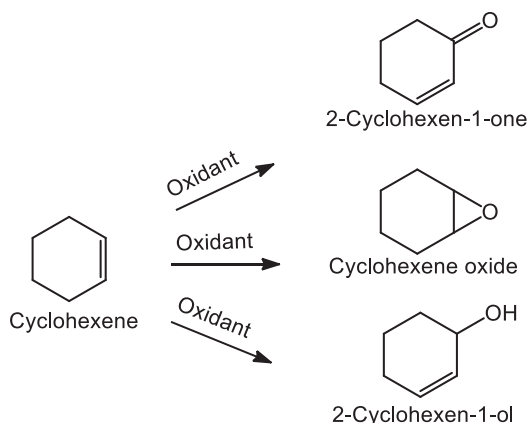


Fig. 1. The proposed reaction scheme for the selective oxidation of cyclohexene.

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