



Gold nanoparticles stabilized by task-specific ionic complexes: Quasi-homogeneous catalysts with self-separating nature for aerobic epoxidation of styrene



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ARTICLE INFO

Article history:

Received 3 July 2014

Revised 13 August 2014

Accepted 14 August 2014

Available online 23 September 2014

Keywords:

Gold nanoparticles
Imidazolium cations
Self-separation
Epoxidation
Oxygen

ABSTRACT

A series of imidazolium cation-based task-specific ionic complexes (TSICs) containing polyethylene glycol (PEG) chains and organic moieties with affinity to Au species were synthesized to stabilize gold nanoparticles (GNPs). With toluene as reaction media, the resultant GNP/TSIC catalysts showed a unique thermoregulated self-separating nature in the dioxygen-mediated epoxidation of styrene. The effects of PEG chain length and operational variables in the epoxidation on the catalytic performance of GNP/TSIC catalysts were investigated systematically. It was found that extending the PEG chain was conducive not only to the formation of small and well-dispersed GNPs but also to the fabrication of GNP/TSIC catalysts with apparent thermoregulated self-separating nature. Under optimum operational variables, a GNP/TSIC catalyst based on a vinyl-functionalized TSIC containing a PEG6000 chain achieved 32.9% styrene conversion with 72.0% selectivity to the epoxide; meanwhile, relevant turnover frequency was as high as 2.47 mol(Au)g⁻¹h⁻¹. Moreover, the catalyst could be reused four times without significant loss of activity.

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1. Introduction

Gold was long considered to be “catalytically dead,” but since 1985, triggered by seminal reports on unexpected high catalytic performance of gold-based catalysts in the hydrochlorination of acetylene [1] and the oxidation of carbon monoxide at low temperatures [2], catalysis based on gold nanostructures has become a highly active field. In contrast to bulk gold, more reactive orbitals and altered electronic band structures, derived from fewer nearest-neighbor atoms, impart unique catalytic properties to nanostructured gold catalysts [3,4]. Nowadays, nanostructured gold catalysts have been demonstrated to be very highly active in many important industrial processes [5,6], especially in a range of selective oxidation transformations [7,8]. Gold nanostructures are

resistant to adsorption of partial oxidation products; consequently, they not only have high selectivity to target products but also are less prone to overoxidation and self-poisoning in selective oxidation reactions [9,10]. This delicate balance between oxidation power and relatively weak interaction with partial oxidation products distinguishes nanostructured gold catalysts from palladium- or platinum-based oxidation catalysts. It should be noted that some nanostructured gold catalysts have exhibited excellent catalytic performance in dioxygen- [11,12] or hydrogen peroxide-mediated [13,14] selective oxidation of hydrocarbons, which implies that nanostructured gold catalysts may be a class of potential “green” oxidation catalysts.

While the origin of active sites associated with nanostructured gold catalysts is still being debated [15], due to the fact that it is very difficult to structurally characterize active sites on or near gold nanostructures, numerous studies have suggested that gold atoms with highly coordinative unsaturation play a crucial role in catalyzing selective oxidation reactions [7,8]. Apparently, gold nanoparticles (GNPs) are a kind of easily obtained gold nanostructure that contains a high ratio of undercoordinated atoms to the total atoms. Thus, aside from a few examples describing layered gold [16] or nanoporous gold [10,17,18], most nanostructured gold

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catalysts reported focus on GNPs, especially those with particle size less than 10 nm [19]. Owing to their low melting point and high surface free energy, GNPs are, in the absence of space confinement, vulnerable to agglomeration during liquid phase selective oxidation reactions [20]. In this context, supports/stabilizers are normally necessary in the fabrication of GNP catalysts to protect GNPs from aggregation and, consequently, to preserve catalytic activity. Solid supports have generally been relied on in fabricating GNP catalysts and have developed from initial metal oxides and carbons to recent organic–inorganic hybrid mesoporous silicas [13,14,21,22], polymers [23,24], natural crystals [25,26], carbon nanotubes [27], etc. Just as with conventional heterogeneous supported catalysts, solid supports facilitate the separation and reuse of GNP catalysts; however, heterogeneous supported GNP catalysts could suffer from mass-transfer limitation and/or potential lack of access of substrates to catalytically active sites.

More recently, quite a few reports have become available describing the preparation of so-called colloidal GNP catalysts without any solid support and the relevant catalytic performance in a series of liquid phase selective oxidation reactions [28,29]. Such solid support-free GNP catalysts often use special stabilizers that make the catalysts miscible with the corresponding reaction media. In this context, GNPs with intrinsic catalytic activity can themselves be recognized as quasi-homogeneous catalysts [30]. Theoretically, owing to their higher active surface area and lower mass-transfer limitation, colloidal GNP catalysts could offer higher activity than heterogeneous supported GNP catalysts in liquid phase selective oxidation reactions, and sometimes this has been demonstrated [31,32]. Generally, the stabilizers used in most colloidal GNP catalysts are organic compounds including poly(*N*-vinyl-2-pyrrolidone) (PVP) [33,34], poly(vinyl alcohol) (PVA) [35,36], dendrimers [37], organosiloxanes [31], and ionic liquids [38,39], which impart a quasi-homogeneous nature to the colloidal GNP catalysts, but result in elevated difficulties in the separation and reuse of the catalysts. Some special methods (for example, nanofiltration [34]) are needed to accomplish the separation of the catalysts. Thus, it is still highly desirable to develop efficient colloidal GNP catalysts with easy separability.

Task-specific ionic liquids/ionic complexes (TSILs/TSICs) [40,41] seem well positioned to address the challenges of developing efficient colloidal GNP catalysts capable of easy catalyst recovery and product isolation, due to the facts that their miscibility in given solvents can be conveniently controlled by a sophisticated choice of cations' side chains and/or anions and that additional functional groups with specific properties can easily be incorporated into their structures as part of cations and/or anions, bringing versatile task-specific capabilities to them. Moreover, low interfacial tension of these ionic complexes leads to a high nucleation rate, allowing the formation of very small nanoparticles because of rather weak Ostwald ripening [42,43]. Based on the concept of "one-phase catalysis and two-phase separation" [44] and our previous work on TSIL-stabilized colloidal GNP catalysts [32,38,39] and TSIL-conducted tunable separation of homogeneous catalysts [45], a series of imidazolium cation-based TSICs containing polyethylene glycol (PEG) chains and organic moieties with affinity to Au species were synthesized and used to fabricate GNP/TSIC catalysts. With toluene as reaction medium, the resultant GNP/TSIC catalysts showed unique thermoregulated self-separation in the dioxygen-mediated epoxidation of styrene; more specifically, the catalysts performed as quasi-homogeneous catalysts during the epoxidation proceeding at relatively high temperature and become solid after the reaction systems were cooled. Toluene is selected as reaction medium because PEG chains have exhibited apparent thermoregulated phase-transfer behavior in toluene [46], and, fortunately, toluene has been shown to be one of the optimum media for dioxygen-mediated epoxidation of olefins [11,12]. To the best of our

knowledge, despite the fact that there is a single report on thermosensitive GNPs stabilized by complex star polymers [47], this is the first example of thermoregulated self-separating colloidal GNP catalysts that can be operated at relatively high temperature, more favorable for selective oxidation of hydrocarbons.

2. Experimental

2.1. Materials

Imidazole, 1-vinylimidazole, and 3-bromopropylamine hydrobromide were purchased from Alfa Aesar. Anhydrous *t*-butyl hydroperoxide (TBHP) was purchased from Sigma–Aldrich. Hydrogen tetrachloroaurate tetrahydrate and polyethylene glycol (PEG $_n$, $n = 1000, 2000, 4000, \text{ or } 6000$) were purchased from Sinopharm Group Co. Ltd. Other commercially available chemicals were analytical grade reagents from local suppliers. PEGs were dried by azeotropic distillation in toluene and the other chemicals were used as received.

2.2. Preparation of TSICs

The procedures for the preparation of the imidazolium cation-based TSICs containing PEG chains and vinyl or amine moieties are outlined in Scheme 1.

2.2.1. Synthesis of polyethylene glycol dichloride with various chain lengths (PEG $_n$ -Cl $_2$)

PEG $_n$ -Cl $_2$ ($n = 1000, 2000, 4000, \text{ or } 6000$) was synthesized according to a modified procedure reported elsewhere [48]. In brief, 5 mmol of PEG $_n$ ($n = 1000, 2000, 4000, \text{ or } 6000$) and 20.0 ml of anhydrous toluene were charged in a 100-ml three-neck round-bottomed flask equipped with a reflux condenser and a magnetic stirrer, followed by dropwise addition of 3.60 ml of thionyl chloride in a period of 40 min; then the resultant mixture was heated to 90 °C for 24 h under nitrogen. The obtained mixture was cooled to room temperature and evaporated until dry. The residue obtained was dissolved in a small amount of dichloromethane and precipitated with a large excess of cold diethyl ether. Filtration and drying under reduced pressure gave the desired PEG $_n$ -Cl $_2$. **PEG1000-Cl $_2$** (92% yield) FT-IR (KBr): 2945, 2865, 2745, 1459, 1351, 1298, 1252, 1109, 946, 851, 745, 663 cm $^{-1}$; **PEG2000-Cl $_2$** (90% yield) FT-IR (KBr): 2943, 2882, 2741, 2695, 1466, 1362, 1279, 1238, 1145, 1113, 947, 842, 662 cm $^{-1}$; **PEG4000-Cl $_2$** (90% yield) FT-IR (KBr): 2945, 2886, 2740, 2696, 1467, 1345, 1280, 1238, 1105, 962, 843, 667 cm $^{-1}$; **PEG6000-Cl $_2$** (89% yield) FT-IR (KBr): 2944, 2886, 2740, 2696, 1472, 1343, 1278, 1240, 1148, 1105, 961, 843, 667 cm $^{-1}$.

2.2.2. Synthesis of vinyl-functionalized TSICs with various PEG chain lengths (PEG $_n$ -VICs)

PEG $_n$ -VICs ($n = 1000, 2000, 4000, \text{ or } 6000$) were synthesized using a modified recipe reported recently [49]. Initially, 40 mmol of 1-vinylimidazole, 10 mmol of the aforementioned PEG $_n$ -Cl $_2$, and 25.0 ml of anhydrous ethanol were charged in a 100-ml three-neck round-bottomed flask equipped with a reflux condenser and a magnetic stirrer, and then, the obtained mixture was stirred at 80 °C for 96 h (PEG1000-Cl $_2$), 120 h (PEG2000-Cl $_2$), or 168 h (PEG4000-Cl $_2$, PEG6000-Cl $_2$) under nitrogen. After removal of ethanol in vacuum, the resultant solid residue was dissolved in a small amount of dichloromethane and precipitated with a large excess of cold diethyl ether. After being filtered, the filter residue was dried at 65 °C under vacuum, yielding PEG $_n$ -VICs (see the Supplementary Information for the detailed attribution of NMR resonances and FT-IR absorption bands). **PEG1000-VIC**

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