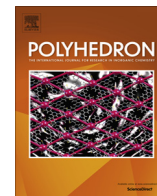




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Water-compatible gold and silver nanoparticles as catalysts for the oxidation of alkenes

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This paper is dedicated to Emeritus Professor Martin A. Bennett on the occasion of his 80th birthday.

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ABSTRACT

Water-compatible Ag/Au nanoparticles (NP) catalyze the liquid-phase oxidation of 1,1-diphenylethylene to afford benzophenone, the product of oxidative cleavage, and 1,1-diphenylepoxyde. The metal nanoparticles are surface functionalized with tannic acid and/or citrate and have diameters of 10–12 nm. By proper selection of the reaction conditions, percent conversions/distributions of 85–100% of 1,1-diphenylethylene can be achieved at 90 °C using water as a solvent and TBHP (tert-butylhydroperoxide) as the co-oxidant. In addition, these nanoparticles have been further supported on functionalized silica to improve their stability and recyclability in this oxidation process. Conversions of up to 100% to benzophenone could be obtained with 1.5 mol% Au or Ag nanoparticles (10 nm) supported on functionalized silica. The supported NP could be recycled and re-used without significant catalytic activity loss for three runs.

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1. Introduction

During the last two decades there has been much interest in finding new and less toxic metal-based oxidation catalysts, with reports that have been compiled in a number of recent reviews [1–10]. Research has been focused on developing highly selective and/or recoverable catalysts which employ oxygen or air as oxidants. While not all new oxidation catalysts have been able to fulfill all the above features, gold compounds and nanoparticles have been proven as an excellent alternative to other classical metal-based oxidation catalysts, and have been successfully used in heterogeneous [11–16] and to a lesser extent in homogeneous oxidations [13–18]. In contrast, oxidations of alkenes with silver compounds in homogeneous conditions have been less explored [12,19]. One relevant oxidation reaction is the oxidative cleavage of C=C double bonds to carbonyl compounds (usually achieved by stoichiometric oxidation or ozonation). In 2006, Shi and

co-workers reported the oxidative cleavage of alkenes to form ketones and aldehydes with AuCl₃/neocuproine in water at 90 °C with TBHP (tert-butylhydroperoxide) as the oxidant (Scheme 1) [20]. Our group reported that gold(I) and especially silver(I) complexes containing a tripodal bis(imidazole) thioether ligand, could perform this oxidative cleavage in toluene [21].

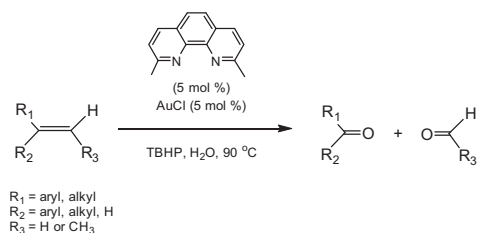
Liu and co-workers synthesized fully substituted butenolides via a cascade reaction for the cleavage of a carbon–carbon triple bond involving: (a) gold-catalyzed addition of an oxygen nucleophile to the triple bonds in (Z)-enynols and, (b) subsequent oxygen-assisted oxidative cleavage of the exo-enolic double bond [22].

In the cases of the oxidative cleavage of alkenes with the Au(I) and Ag(I) compounds [20,21], we wondered if the active catalyst could be nanoparticles generated under reaction conditions and we set to explore the catalytic activity of Au and Ag NP in H₂O. We report here on the use of commercially available water-compatible Ag/Au nanoparticles for the liquid-phase oxidation of 1,1-diphenylethylene in H₂O at 90 °C with TBHP as oxidant. The oxidation products are benzophenone, product of the oxidative cleavage, and 1,1-diphenylepoxyde (Scheme 2). We also describe catalytic studies with the nanoparticles further supported on functionalized silica in order to improve the recyclability of the systems.

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Scheme 1. Oxidative cleavage of alkenes with a gold(I) catalyst [20].

2. Experimental

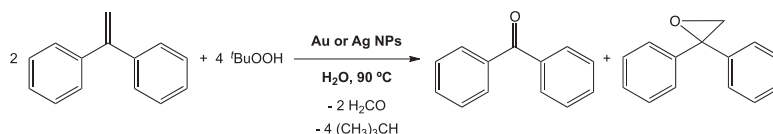
2.1. General procedure

The unsupported water suspended metal nanoparticles employed are surface functionalized with tannic acid and/or citrate in the case of gold and citrate surface groups in the case of silver and have dimensions of 10–12 nm. The nanoparticles used are available commercially from nanoComposix (products AuB10, AuB12 and AgCB10 for gold at 10 and 12 nm and silver respectively). 1,1-diphenylethylene was purchased from Sigma Aldrich. All purchased reactants were used without further purification. Reaction and work-up solvents were purchased from Fisher Scientific (ACS Grade). Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc., were kept over molecular sieves (3 Å, beads, 4–8 mesh). NMR spectra were recorded using a Bruker

AV400 (^1H NMR at 400 MHz, $^{13}\text{C}\{^1\text{H}\}$ NMR at 100.6 MHz). Chemical shifts (δ) are given in ppm using CDCl_3 as the solvent, and spectra was recorded at 25 °C. ^1H and ^{13}C NMR resonances were measured relative to solvent peaks with tetramethylsilane = 0 ppm. Coupling constants J are given in hertz. Nanoparticles were characterized by TEM and UV–Vis spectroscopy as well as ICP–MS for metal concentration by nanoComposix.

2.2. Catalytic oxidation procedure for unsupported nanoparticles

To 1.5 ml of deionized H_2O , TBHP (2.1 equiv.) and the alkene (1,1-diphenylethylene) were added at room temperature. Solutions of metal nanoparticles in water were subsequently added (different concentrations, see Tables 1–4 for mol per cent values). The reaction mixture was stirred under reflux at 90 °C (different times were studied, see Tables 1–4). After the reaction finished and the flask was cooled to room temperature, the aqueous layer was extracted with diethyl ether (3×20 mL). The combined organic layers were washed with a saturated sodium bisulfite solution (3×10 mL) followed by deionized H_2O (3×20 mL), and dried over MgSO_4 overnight. The solution was then filtered and concentrated under vacuum. The product obtained was analyzed by ^1H NMR spectroscopy. Ketone and epoxide (Scheme 2) were observed in different percent conversions depending on the reaction conditions (Tables 1–4). Diagnostic signals in ^1H NMR spectra (CDCl_3): 1,1-diphenylethylene 5.5 ppm (2H, s, CH_2), 7.6–7.3 ppm (10H, m, 6CH); benzophenone 7.8 ppm (4H, m, 4CH); 1,1-diphenylepoxide 4.84 ppm (2H, s, CH_2).



Scheme 2. Oxidative cleavage of 1,1-diphenylethylene catalyzed by Au or Ag NP.

Table 1
Oxidations with 1 mol% of gold nanoparticles of size 10 nm (entries 1–4) and 12 nm (entries 5–8).^a

Entry	Type of NP	[cat] mol%	Time (h)	Conversion (%)			Std dev
				To ketone	To epoxide	Total	
1	10 nm Au	1	18	85	15	86	4
2	10 nm Au	1	5	85	15	69	0
3	10 nm Au	1	2	67	33	71	4
4	10 nm Au	1	1	65	35	39	12
5	12 nm Au	1	18	79	21	90	3
6	12 nm Au	1	5	78	22	87	0
7	12 nm Au	1	2	66	34	63	2
8	12 nm Au	1	1	62	38	54	2

^a Reaction conditions: 0.5 mmol diphenylethylene, 1.05 mmol TBHP, H_2O , 90 °C. Conversion determined by ^1H NMR spectroscopy. Values given are an average of two reactions. The standard deviation is given for the conversion of ketone.

Table 2
Oxidations with gold nanoparticles of size 12 nm (18 h).^a

Entry	Type of NP	[cat] mol%	Time (h)	Conversion (%)			Std dev
				To ketone	To epoxide	Total	
1	12 nm Au	1	18	79	21	90	3
1	12 nm Au	2	18	83	17	70	3
2	12 nm Au	5	18	88	12	84	0

^a Reaction conditions: 0.5 mmol diphenylethylene, 1.05 mmol TBHP, H_2O , 90 °C. Conversion determined by ^1H NMR spectroscopy. Values given are an average of two reactions. The standard deviation is given for the conversion of ketone.

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