



Dioxygen oxidation of 1-phenylethanol with gold nanoparticles and *N*-hydroxyphthalimide in ionic liquid

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ABSTRACT

Gold nanoparticles (Au-NPs) of 8 nm average diameter were obtained by thermal reduction under nitrogen from KAuCl_4 in the presence of *n*-butylimidazol dispersed in the ionic liquid (IL) 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($\text{BMIm}^+\text{BF}_4^-$). Characterization of the Au-NP was done by transmission electron microscopy (TEM) and dynamic light scattering (DLS). Catalytic activities of the Au-NP/IL dispersion were evaluated in the oxidation of 1-phenylethanol at 100 and 160 °C under 4 bar pressure of dioxygen in a base-free system. Au-NP in combination with the radical initiator *N*-hydroxyphthalimide (NHPI) showed good conversion and selectivity for the oxidation of 1-phenylethanol to acetophenone through formation of an α -hydroxy carbon radical. The concomitant side products di(1-phenylethyl)ether and di(1-phenylethyl)peroxide were rationalized by an equilibrium due to the IL matrix of the α -hydroxy carbon radical with the 1-phenylethoxy radical. Maximum turnover number was ~ 5200 based on the total number of moles of gold but a factor of about six larger, $\text{TON} \approx 31\,300$, when only considering the Au-NP surface atoms. The fraction (N_s/N_T) of exposed surface atoms ($N_s \approx 2560$) for an average 8 nm Au-NP (having $N_T \approx 15\,800$ atoms in a ~ 17 -shell icosahedral or cuboctahedral particle) was estimated here as 0.16.

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1. Introduction

Selective oxidation of alcohols to carbonyl compounds is a fundamental transformation in organic synthesis because the target molecules can be obtained directly in one-pot sequences. Alcohols are important precursors for various chemicals and in particular, the oxidation of alcohols and polyols is of interest owing to the large array of biological hydroxy-derivatives [1–3]. Choice of the oxidants determines the practicability and efficiency of the oxidation reactions. Oxidants, like MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ produce toxic, environmentally and economically unacceptable by-products or like NaOCl have a low (≤ 30 wt.%) active oxygen content. In this context, O_2 (or air) is the most attractive oxidants because of its high contents of active oxygen species (100% for dioxygenase-type, 50% for monooxygenase-type) and co-production of only water.

Nanoparticles (NPs) are of high interest in catalysis [4–6]. The small size of nanoparticles results in a large fraction of surface atoms [7]. Interaction of unprotected small particles will, however lead to agglomeration or aggregation from the cohesive surface

energy [8]. As a result of their colloidal instability, many nanoparticles need to be stabilized via additional (capping) agents such as surfactants or polymers, which provide a steric, electrostatic or electrosteric particle stabilization [9]. For catalytic applications of NPs strong surface protection is, however, undesirable as it hinders substrate access and interaction with the surface catalytic sites. Instead ligand-free NPs should be advantageous for a high activity. Ionic liquids (ILs) can stabilize M-NPs on the basis of their ionic nature [10], high polarity, high dielectric constant and supramolecular network without the need of additional protective ligands [11]. ILs therefore function both as stabilizer and solvent for the preparation of small (< 5 nm) and (generally) kinetically stabilized M-NPs [4,12,13].

The past decade has seen an explosive growth in catalytic reactions studied in ILs. Often the IL enables more efficient reactions compared with standard organic solvents and catalysts show good or even enhanced activities when applied in ionic liquids [14–16]. ILs are interesting in the context of green catalysis [17] which requires that catalysts be designed for easy product separation from the reaction products and multi-time efficient reuse/recycling [18]. The Pd-metal-catalyzed oxidation of benzyl alcohol with 1 atm O_2 in the IL BMIm^+X^- gave good conversion to benzaldehyde, albeit only for $\text{X} = \text{BF}_4$ and not for $\text{X} = \text{Cl}$ or Br and with Pd amounts of equal or larger than 2.8 mol% [19].

Oxidation by gold is of timely interest for green processes requiring stable, selective and non-toxic heterogeneous catalysts, as well

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as air or O₂ as oxidants [20–22]. Gold is cheaper than platinum, palladium and most other noble metals used as catalyst. One of the unique features of gold catalysis is the kinetic aspect of correlating the turnover frequency strongly to the size of metallic gold particles. In particular, many investigations on the liquid-phase oxidation of polyols, alcohols and carbohydrates indicate that only small gold particles are catalytically active [23]. A size threshold in gold catalytic activity has been found resulting in complete inactivity for particles with diameters >~2 nm [20]. Compared to other common catalysts, like the platinum group metals, the outstanding properties of gold catalysis are also represented by high selectivity which allows discrimination within chemical groups and geometrical positions, leading to superior yields in the desired products. Among many examples, glycols can be oxidized to monocarboxylates [24], and unsaturated alcohols to unsaturated aldehydes [25]. From its biocompatibility, availability and easy recovery, gold appears as an exciting catalyst for sustainable processes based on the use of clean reagents, particularly O₂. Considering the influence of various parameters in the aerobic oxidation of alcohols by gold based catalysts, it can be concluded that a prominent role in the activity and selectivity is played by the solvent [26].

Unsupported nanogold was described for the aerobic oxidation of stilbene and cyclohexene in methylcyclohexane [27] and the aerobic oxidation of alcohols [28]. Gold nanoparticles have been used mostly as supported catalysts for oxidation applications [14,20,30,29,26]. The unique catalytic activity of supported Au nanoparticles has been ascribed to various effects including thickness/shape, the metal oxidation state, and support effects [31]. Benzyl alcohol is oxidized selectively to benzaldehyde with high yield by molecular oxygen over a reusable nano-sized gold catalyst supported on U₃O₈, MgO, Al₂O₃ or ZrO₂ in the absence of any solvent with only little formation of benzylbenzoate [32].

From the viewpoints of atom economy and environmental concern, developing noble metal catalysts and using molecular oxygen or air as the oxidant prevail as an attractive green technology [33,34]. Here we report to the best of our knowledge for the first time oxidation of an alcohol with gold nanoparticles (Au-NPs) in an ionic liquid (Scheme 1).

2. Experimental

2.1. Materials and instrumentation

KAuCl₄ was obtained from STREM, *n*-butylimidazole (p.a.) from Aldrich, *N*-hydroxyphthalimide (NHPI) from ACROS, the ionic liquid (IL) 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMIm⁺BF₄⁻) from IoLiTec (H₂O content << 100 ppm; Cl⁻ content << 50 ppm). All manipulations were done by using Schlenk techniques under nitrogen. The ionic liquid was dried under a high vacuum (10⁻³ mbar) for several days to avoid hydrolysis of BMIm⁺BF₄⁻ to HF [18,35–37].

FT-IR (Fourier transform infrared) measurements were carried out on a Bruker TENSOR 37 IR spectrometer in a range from 4000 to 500 cm⁻¹ with ATR technique.

A Malvern Zetasizer Nano-ZS was used for the dynamic light scattering (DLS) measurements working at 633 nm wavelength. The resolution of the DLS instrument is 0.6 nm. Care was taken for choosing the right parameters, such as the index of refraction of Au (0.11) with absorption of 0.1 at this wavelength. Samples were prepared by dilution of the metal/IL dispersion (10 μL; 1.0 wt.% of Au) in *n*-butylimidazole (2 mL, 99% p.a.; particle free) and was placed in a glass cuvette before measurement.

HAADF-STEM (high angle annular dark field scanning transmission electron microscopy) images were taken with FEI TECNAI G² F

20 (S)TEM and FEI TITAN 80-300 probe CS-corrected STEM. All samples for HAADF-STEM were prepared by dropping a small amount of Au-NP/IL dispersion on a carbon coated copper grid. After 5 min the excess of the IL was removed by dipping the grid into a water bath for 2 min. Finally the grid was plasma cleaned for 10 s.

Gas chromatography measurements were conducted using a Perkin Elmer headspace GC HS6 with a flame ionization detector (FID) and a PEG capillary column (25 m long × 0.32 mm inner diameter × 1.0 μm film thickness). The GC program used was: oven temperature 120 °C, injector temperature 170 °C, carrier gas N₂ pressure 200 kPa. The conversion was analyzed by adding a drop of the mixture into a headspace GC sample vial with 1 mL of water. The addition of water as a non-electrolyte can enlarge the activity coefficient of organic components; thereby increases their detection sensitivity through the increase in peak area. The FID does not detect the water itself [38]. In order to verify the results of the headspace GC analyses we isolated the reaction products from selected experiments using standard procedures and confirmed their purity by ¹H NMR. Conversion and selectivity were calculated with respect to the substrate. The products were identified with Thermo Trace DSQ GC-MS and ¹H NMR. ¹H NMR spectra were collected on a Bruker Avance DRX 500 spectrometer (500 MHz) or a Bruker Avance DRX 200 spectrometer (200 MHz) as CDCl₃ solutions.

2.2. Synthesis of gold nanoparticles in ILs [12]

Au-NP was prepared by thermal decomposition and reduction from KAuCl₄ in an ionic liquid (cf. Scheme 1) under nitrogen in a glass vessel which was connected to an oil bubbler. In a typical experiment KAuCl₄ (57.6 mg, 0.152 mmol) was dissolved/dispersed (during 48 h) under nitrogen at room temperature in the presence of *n*-butylimidazole (1.5 equiv. for each Cl atom, 0.914 mmol) in the ionic liquid 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMIm⁺BF₄⁻) (3.0 g, 2.5 mL, density 1.2 g/mL). The solution was slowly heated to 230 °C for 18 h under magnetic stirring. The solution color immediately changed from yellow to dark red (dark brown-red), indicating the formation of gold nanoparticles. The decomposition process gave a 1.0 wt.% or 60.8 μmol/mL dispersion of gold (30 mg in 3.0 g IL). During the decomposition process, a white haze of *n*-butylimidazolium chloride was formed. After cooling to room temperature under nitrogen, an aliquot of the ionic liquid was collected under nitrogen atmosphere for TEM and dynamic light scattering (DLS) characterization.

2.3. Catalytic dioxygen oxidation of alcohol with Au-NP/IL

The oxidation reactions were carried out in a glass inlay of a 100 mL steel autoclave. The autoclave was conditioned by evacuation and re-filling with dioxygen. All autoclave loading was carried out under air. In a typical experiment, 5.0 mL (41.3 mmol) of 1-phenylethanol was added to the reactor with 0.1 mL Au-NP/BMIm⁺BF₄⁻ dispersion (6.1 μmol Au) and NHPI (1 mmol). After purging with O₂, the reactor was pressurized to 4 bar and placed in a thermostated oil bath at a chosen temperature of 100 or 160 °C (see Table 1). Stirring rate was 850 rpm. The O₂ consumption over time was monitored online with a Büchi pressflow gas controller (Büchi pbc). After 24 h the reactor was depressurized and the product mixture was analyzed by gas chromatography and ¹H NMR as follows: (i) by taking a sample with a Pasteur-pipette from the reaction mixture without removing the NP/IL dispersion and after adding 1 mL water injecting it into headspace GC; (ii) by evacuating the substrate/product from the NP/IL under vacuum (0.003 mbar, 200 °C) into a clean cold trap and injecting into headspace GC; (iii) by removing the substrate/product from NP/IL by extraction with petroleum ether or diethyl ether (3 × 1 mL) and

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