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Research Note

Efficient aerobic oxidation of alcohols in water catalysed by microgel-stabilised metal nanoclusters

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Abstract

Noble metal nanoclusters stabilised by *N*,*N*-dimethylacrylamide-based soluble cross-linked polymers (microgels) have been prepared and tested as catalysts in the selective oxidation of secondary alcohols to the corresponding carbonyl compounds with molecular oxygen in water. Pd nanoclusters turned out to be superior catalysts compared with nanoclusters of other noble metals, such as Pt or Au; they are efficient (TOF up to 70 h^{-1}) and easily recoverable by simple extraction of the reaction product from the aqueous phase.

Keywords: Alcohol; Microgel; Oxidation; Dioxygen; Water; Palladium; Platinum; Gold

1. Introduction

The current surge of interest for the applications of nanosized matter (nanotechnology) has generated a strong impulse toward the development of methods for the controlled preparation of nanoscopic building blocks composed of various materials [1]. In particular, much success has been achieved in the synthesis of metal nanoparticles [2], to the point where some of these particles have become commercially available [3]. The availability of such synthetic methods has in turn promoted extensive studies on the possible applications of these materials, including their catalytic application [4]. Size- and shape-controlled metal nanoparticles ("metal nanoclusters") are in fact expected to exhibit superior catalytic performance over randomly sized and shaped particles, at least for certain reactions. A powerful demonstration of this principle is the recently developed process for CO oxidation by gold nanoclusters, where the best catalytic activities are achieved with nanoparticles of around 3 nm [5].

The most commonly used synthetic strategy for the controlled preparation of metal nanoclusters is arguably their generation in solution, starting from metal atom precursors in the presence of a stabiliser able to interact with the metal. The stabiliser prevents agglomeration and controls the growth of the metal nanoparticles to a definite, possibly predetermined, size and shape [1–4]. Various methods for generating the metal atom precursors have been proposed in the literature, as have various stabilizers, including solvent molecules, ion pairs, surfactants, ligands, dendrimers, polymers, and polymer assemblies [1–4,6]. The resulting stabilised metal nanoclusters dispersed in solution can be used as catalysts as such or subsequently heterogenised on solid supports by different means (e.g., surface adsorption, covalent anchoring, embedding by sol–gel techniques) [7].

We [8] and others [9,10] have recently introduced microgels as stabilisers for metal nanoclusters. Microgels [11] are nanoscopic objects in themselves, in that they are cross-linked, globular-shaped macromolecules 10^1–10^2 nm in size. Such macromolecules can be prepared by slight modification of standard polymerisation techniques and resemble in their structure and behaviour soluble cross-linked biological macromolecules, such as proteins. Microgels build up low-viscosity, stable solutions in appropriate solvents and can be easily isolated therefrom by precipitation, ultracentrifugation, or ultrafiltration. Remarkably, they can be tailored to bear chemical functionalities able to interact with metal ions or complexes, which are subsequently reduced inside the microgel to yield metal nanoclusters.

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Microgel-stabilised, size-controlled metal nanoclusters have recently found promising applications in fields ranging from catalysis to drug delivery and materials science [8–10]. In particular, we have previously demonstrated their usefulness as catalysts in C–C coupling reactions, such as Heck and Suzuki couplings [8b,8c]. We have now extended the application of microgel-stabilised metal nanoclusters to the catalysis of the selective oxidation of secondary alcohols to the corresponding carbonyl compounds with molecular oxygen in water [12]. We were prompted to study this reaction by a recent report of Uozumi and Nakao claiming high catalytic activity of Pd colloids dispersed in an amphiphilic insoluble polymer support [13]. Apparently, using an amphiphilic support helped overcome the most serious drawback of this reaction, the low water solubility of many alcohol substrates. The support was supposed to preferentially absorb the alcohol substrate, thereupon achieving a relatively high substrate concentration in the microenvironment surrounding the polymer-supported, catalytically active metal colloids. It is important to note that water is almost the only solvent currently deemed suitable for the industrial application of this catalytic process, because it avoids the hazards associated with the use of oxidisable organic solvents under oxygen pressure [12d]. We have argued that using a *soluble* amphiphilic support, coupled with more stringent control of the size and size distribution of the catalytically active metal nanoclusters, should provide a catalyst with enhanced catalytic activity.

2. Experimental

Solvents and chemicals were of reagent grade and were used as received, apart from the monomers for microgel synthesis, which were freshly distilled to free them from inhibitors before use.

2.1. Microgel preparation

Monomers were mixed in the desired ratios (Table 1) in a round-bottomed flask. The resulting mixtures (5 g) were diluted with cyclopentanone (45 g). Azobis(isobutyronitrile) (AIBN) (0.18 g, 3% w/w with respect to the monomer mixture) was then added. The resulting solution was degassed, put under nitrogen, and placed for 48 h in a thermostatted oven preheated to 80 °C. The polymerisation solution was concentrated to about half of the original volume and subsequently poured in the fivefold volume of diethylether under efficient stirring. The precipitated solid was filtered off and dried under vacuum to constant weight. Isolated yields were about 80% in all cases.

2.2. Preparation of microgel-stabilised Pd or Pt nanoclusters

In the general procedure, microgel (1 g) was dissolved in dichloromethane (80 mL) under an inert atmosphere. Then $Pd(OAc)_2$ (50 mg) or $PtCl_2(CH_3CN)_2$ (78 mg) was added, and the resulting solution was stirred at room temperature overnight. Subsequently, $NaHBEt_3$ (2.2 mL 1 M solution in THF, 10 eq. with respect to metal) was added, and the resulting solution was stirred at room temperature for 1 day. The solution was concentrated to about half of the original volume, and the nanocluster-containing microgel was subsequently precipitated by pouring the solution in the fivefold volume of diethylether under efficient stirring. Isolated yields were about 90% in all cases.

Table 1
Composition of the functionalised microgels employed in this work[a]

Microgel	DMAA (mol%)	EDMA (mol%)	DMAEMA (mol%)
M5	85	5	10
M7.5	82.5	7.5	10
M10	80	10	10
M10b	40	10	50
M20	70	20	10

[a] Polymerisation conditions: 3% w/w AIBN, 10% w/w monomer mixture in cyclopentanone, 80 °C, 48 h.

2.3. Preparation of microgel-stabilised Au nanoclusters

Microgel **10b** (1 g; Table 1) was dissolved in ethanol (80 mL) under an inert atmosphere. Then $AuCl_3$ (61 mg) was added, and the resulting solution was stirred at room temperature for 1 day. The solution quickly changed colour from pale yellow to dark purple. The solution was concentrated to about half of the original volume and then poured in the fivefold volume of petroleum ether under efficient stirring. The nanocluster-containing microgel separated as a viscous oil, which was subsequently redissolved into the minimum amount of dichloromethane and precipitated from petroleum ether. The isolated yield was 23% (not optimised).

2.4. Transmission electron microscopy measurements

Samples for transmission electron microscopy (TEM) measurements were prepared by placing a drop of a solution of microgel-stabilised metal nanoclusters in dichloromethane on a carbon-coated copper grid, followed by solvent evaporation at room temperature. TEM micrographs were taken at CIGS-University of Modena, Italy, with a JEOL 2010 microscope with GIF operating at an accelerating voltage of 200 KeV. Average metal nanocluster sizes and size distributions were computed as the average of at least 100 particles taken from different fields.

2.5. Catalytic tests

The catalytic tests were run in a three-necked, round-bottomed flask equipped with a reflux condenser and a gas inlet. Typical procedure: a solution of microgel-stabilised metal nanoclusters (50 mg) in distilled water (4 mL) was placed in the flask. Then 1-phenylethanol (0.13 mL, 100 eq. with respect to the metal) was added, and the apparatus was evacuated and flushed with dioxygen a couple of times, after which it was connected to a dioxygen-filled balloon. The reaction was started by placing the flask into an oil bath preheated to 100 °C and initiating efficient magnetic stirring. After the given reaction time, the