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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

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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

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.

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.

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 reaction solution was transferred into a separation funnel and extracted with two 2-mL portions of diethylether. The organic layers were combined, and their content in reactant and product was determined by gas chromatography (GC). GC yields were occasionally confirmed by evaporating the organic layers to dryness and determining the yield and purity of the reaction product gravimetrically and by ^{1}H nuclear magnetic resonance. The aqueous phase containing the catalyst was used directly in another reaction cycle after extraction by pouring it back in the reaction flask and adding fresh reagent.

3. Results and discussion

We prepared a series of microgels based on *N*,*N*-dimethylacrylamide (DMAA) with varying cross-linking degree and content of functional comonomer, following our synthetic procedure described previously [8c]. Microgels were prepared from DMAA as the main comonomer, ethylene dimethacrylate (EDMA) as the cross-linker, and *N*,*N*-dimethylaminoethylmethacrylate (DMAEMA) as the functional, metal-binding comonomer. The composition of the monomer mixtures and the polymerisation conditions are reported in Table 1.

The microgels could be conveniently isolated by precipitation as white powders and readily redispersed in water and in many different organic solvents, including alcohols, dialkylamides, nitriles, dichloromethane, acetone, and THF. The microgels were loaded with palladium(II), platinum(II), or gold(III) by letting them react with $Pd(OAc)_2$, with $PtCl_2(CH_3CN)_2$ in dichloromethane, or with $AuCl_3$ in ethanol [8b, 8c]. The reaction was carried out with 0.25 eq. of metal precursor with respect to the available amino groups in the microgel, except for microgel **M10b**, which because of its high number of amino groups had a scaled-down amount (0.05 eq.) of metal precursor. Consequently, the total metal content in the various microgels was set to 2.4% w/w for Pd and 4.2% w/w for Pt and Au.

Reduction of the microgel-bound Pd and Pt precursors with $NaHBEt_3$ yielded solutions of microgel-stabilised metal nanoclusters, which could be easily precipitated from the reaction mixture. The reduction step was not necessary for gold, because the microgel-anchored gold(III) underwent spontaneous reduction under ambient conditions; in this case, the actual reducing agents are probably the polymer-bound trialkylamino groups themselves, which are known to act similarly toward other, less easily reducible metal centers [14]. The obtained powders can be stored and readily redispersed in good solvents for the microgel stabiliser. The resulting solutions were clear and turned out to be stable for months without any observable precipitation of metal.

The average size and size distribution of the microgel-stabilised metal nanoclusters were investigated by TEM; the results are reported in Table 2. Some typical TEM micrographs are shown in Fig. 1. TEM analysis revealed, at variance with other sets of metal nanoclusters stabilised by microgels of a more lipophilic nature [8b], very limited dependence of metal nanocluster size on the cross-linking degree of the microgel. A small decrease in size with increasing cross-linking degree was still observed in Pd, whereas such a dependence virtually disappeared in Pt. Furthermore, the uncontrolled, spontaneous reduction leading to Au nanoclusters yielded, as expected [8a, 8b], much larger nanoparticles than with Pd and Pt. We have very recently been able to overcome this problem by changing the nature of the functional monomer in the microgels; the related results will be reported in due course.

The catalytic tests were initially run under the reaction conditions originally reported by Uozumi and Nakao (water; neutral pH; 100 °C; 1 bar O_2; 1 mol% catalyst) with 1-phenylethanol as poorly water-soluble standard substrate. The catalytic activity determined after 2 h reaction time and normalised for the fraction of surface Pd atoms [15] (Table 3) was found to be almost independent of the Pd nanocluster sample used (i.e., independent of the nanocluster size and of the cross-linking degree of the microgel) and equal to about 70 h^{-1}. The Pd-catalysed oxidation reaction reaches completion after 6 h in all

Table 2
Average size and size distribution of microgel-stabilised metal nanocluster

Sample	Size (nm)
M5-Pd	2.8 ± 0.8
M7.5-Pd	2.3 ± 0.7
M10-Pd	1.9 ± 0.5
M10b-Pd	2.2 ± 0.9
M20-Pd	2.0 ± 0.6
M5-Pt	1.8 ± 0.5
M7.5-Pt	1.9 ± 0.6
M10-Pt	1.7 ± 0.5
M20-Pt	2.0 ± 0.6
M10b-Au	10 ± 4

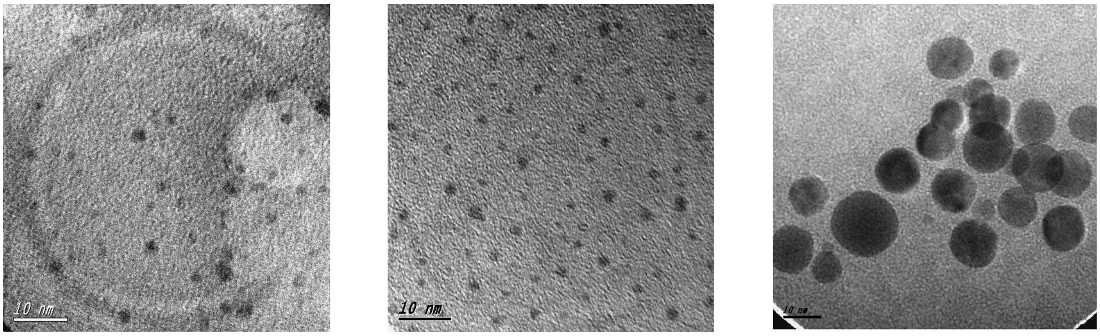

Fig. 1. Representative TEM micrographs of microgel-stabilised metal nanocluster; from left to right: **M5**-Pd, **M5**-Pt, **M10b**-Au.

Table 3
Oxidation of 1-phenylethanol with dioxygen in water catalysed by microgel-stabilised metal nanoclusters[a]

Catalyst	Time (h)	Yield (%)	TOF (h^{-1})[b]
M5-Pd	2	56	70
	6	100	
M7.5-Pd	2	49	52
	6	100	
	2	29[c]	
M10-Pd	2	84	78
	6	100	
M10b-Pd	2	71	75
	6	100	
M20-Pd	2	82	77
	6	100	
M5-Pt	24	12	n.d.
M10b-Au	24	13	n.d.
	24	36[d]	

[a] Reaction conditions: neutral pH, 100 °C, 1 bar O_2, 1 mol% catalyst.

[b] TOF after 2 h of reaction, normalised for the fraction of exposed surface Pd atoms, see [15].

[c] Reaction run under 1 bar of air.

[d] Reaction performed at pH 9.9.

cases (not optimised). Thus, the catalytic productivity of our Pd nanocluster catalysts is significantly superior to that of Uozumi and Nakao's catalyst [13], which needed 20 h at 2 mol% catalyst loading to reach complete conversion. Compared with other recently reported Pd metal catalysts for alcohol oxidations with dioxygen in water, the productivity of our catalysts appears to be higher than that of palladium nanoparticles entrapped in aluminum hydroxide (90% yield after 6 h at 1 mol% catalyst loading) [16a], and slightly lower than that of palladium nanoparticles supported on hydroxyapatite (>99% yield after 24 h with 0.04% catalyst loading) [16b]. Remarkably, the reaction can be also run under 1 bar of air instead of pure oxygen, although in this case the catalytic activity is lower (Table 3).

In contrast to the results obtained with Pd, microgel-stabilised Pt and Au nanoclusters exhibit a much lower productivity under the same reaction conditions, yielding only a low amount of ketone even after 24 h (Table 3). Of course, the unsatisfactory performance of the Au nanoclusters may be at least partially related to their large size. The productivity of the Au nanoclusters can be somewhat enhanced by running the reaction at basic pH. It is in fact known that the reactivity of Au nanoparticles in selective oxidation reactions of this kind increases at basic pH [17], although the reason for this behaviour remains obscure. Indeed, at pH 9.9, the activity of the Au nanoclusters increases significantly, although it is still much lower than that of Pd nanoclusters. Further enhancement of the pH of the reaction solution was not possible, due to the precipitation of catalyst caused by the increased microgel hydrophobicity on deprotonation of the polymer-bound amino groups [8d].

It is possible that even better catalytic productivity can be achieved with smaller Au nanoclusters. Indeed, very recently the Corma group reported on 2–5 nm gold nanoclusters supported on nanocrystalline ceria; they took advantage of a collaborative effect between metal and support to oxidize alcohols under solventless conditions as well as in water (at basic pH) with very high efficiencies [18]. We are currently aiming to obtain smaller Au nanoclusters and test them in these reactions.

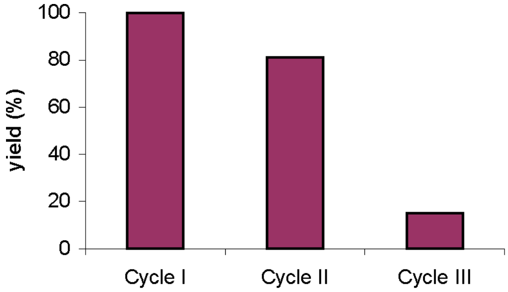

Fig. 2. Recycling of Pd nanoclusters stabilised by microgel **M7.5**; reaction conditions: water, neutral pH, 100 °C, 1 bar O_2, 5 h, 1-phenylethanol as substrate.

After reaction, the product can be quantitatively extracted from the reaction mixture with diethylether, whereas the catalyst remains quantitatively (as judged by ICP-AAS analysis of the extract) in the aqueous phase, which can be directly recycled. We investigated the variations in catalytic performance of one microgel-stabilised Pd catalyst (prepared from microgel **M7.5**) over three reaction cycles of 5 h each. We observed only a small drop in the reaction yield in the second cycle, and a more considerable drop in the third cycle (Fig. 2).

This behaviour most probably results from insufficient stability of the microgel-stabilised Pd nanoclusters under the reaction conditions used. Indeed, a significant precipitation of Pd metal from the aqueous phase is observed in the third reaction cycle. We attempted to overcome this problem by decreasing the reaction temperature, but had to realize that this also dramatically reduced the reaction rate; on going from 100 to 80 °C, the normalized TOF after 2 h for Pd nanoclusters stabilised by microgel **M7.5** dropped from 52 to 4.2 h^{-1}. We are currently investigating the mechanisms leading to catalyst decomposition with the aim of rationally improving the structure of the microgel stabilisers.

The reactivity of some other poorly water-soluble secondary alcohols under these conditions was tested using microgel-stabilised Pd nanoclusters prepared from microgel **M10**. Unfortunately, aliphatic secondary alcohols exhibit much lower catalyst productivity than the benzylic ones; 2-octanol and cyclohexanol reach yields after 24 h of only 7 and 10%, respectively. This is not entirely surprising, however, because aliphatic alcohols are known to be much more demanding substrates for this kind of reaction whenever Pd metal catalysts are used, as can be inferred from the literature, including the results of Uozumi and Nakao, which report similar productivities with these substrates for their catalyst [12a,13].

In conclusion, we have shown that microgel-stabilised Pd nanoclusters are remarkably active catalysts for the aerobic oxidation of benzylic secondary alcohols in water. The nanocluster catalyst is readily separated from the reaction products and can be reused, albeit to a limited extent. Work currently in progress is aimed at improving nanocluster reactivity with aliphatic alcohols, as well as nanocluster recyclability.

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