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Microgel-stabilized gold nanoclusters: Powerful "quasi-homogeneous" catalysts for the aerobic oxidation of alcohols in water

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Dedicated to Professor Benedetto Corain in occasion of his 65th birthday

Abstract

Gold nanoclusters of small size (2.5 nm) and narrow size distribution were synthesized in solution using tailor-made soluble cross-linked polymers (microgels) as exotemplates and stabilizers. The resulting microgel-stabilized nanoclusters could be conveniently isolated by precipitation, stored in the solid state, and redispersed in water and polar organic solvents. They were found to exhibit remarkable catalytic activity (average TOF up to 960 h^{-1}) in the aerobic oxidation of benzylic and aliphatic alcohols and also of polyols in water under mild conditions (50–70 °C, 1–3 atm O_2).

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

1. Introduction

Gold can be arguably defined as the catalytic metal of the beginning of the twenty-first century. Indeed, research on gold metal, gold(III) compounds (most notably $AuCl_3$), and gold(I) complexes has permeated nearly all aspects of catalytic chemistry in the course of the last 10 years, with applications including a plethora of different reactions, such as hydrogenations, oxidations, and C–C and C–heteroatom bond-forming reactions [1]. In particular, research on nanosized gold metal catalysts has been actively pursued, because it has been recognized that size- and shape-controlled gold nanoparticles ("gold nanoclusters") [2] exhibit superior catalytic performance compared with 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 supported gold nanoclusters, where the best catalytic activities are achieved with nanoparticles around 3 nm in size [3]. More recently, the importance of the size of gold nanoclusters in determining good activity and/or selectivity has been demonstrated for other reactions as well, most notably in the field of liquid-phase selective oxidations, particularly in the oxidation of carbohydrates and of polyols [4].

Among the synthetic strategies which have been proposed for the preparation of gold nanoclusters [5], the oldest and most commonly used is arguably their generation in solution by reduction of suitable precursors in the presence of a stabilizer (sometimes the reducing agent itself) able to interact with the metal surface and thus prevent agglomeration [6]. By controlling the nature and amount of stabilizer as well as the reduction conditions, it is sometimes possible to direct the growth of gold nanoparticles to a definite size [4b,7,8]. The resulting stabilized gold nanoclusters are dispersed in solution and can be used as catalysts as such [7,8] or subsequently heterogenized on solid supports by different means (e.g., surface adsorption, covalent anchoring, embedding by sol–gel techniques) to prevent their aggregation under reaction conditions [9]. However, immobilization often results in a decrease of the active surface area of the nanoclusters and, in turn, of their specific catalytic activity. Therefore, the stabilization of dispersions of gold nanoclusters under reaction conditions represents a way to finalize their high activity.

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We [10] and others [11–15] have recently introduced microgels as stabilizers for metal nanoclusters. Microgels [16] are nanoscopic objects in themselves, in that they are cross-linked macromolecules with a globular shape, 10^1–10^2 nm in size. Such macromolecules can be prepared by slight modification of standard polymerization techniques and resemble in their structure and behavior soluble cross-linked biological macromolecules, such as proteins. Microgels build up low-viscosity, stable solutions in appropriate solvents and can be easily isolated from these by precipitation, ultracentrifugation, or ultrafiltration. Remarkably, they can be tailored to bear chemical functionalities that can interact with metal ions or complexes, which are subsequently reduced inside the microgel to yield metal nanoclusters. The resulting nanoparticles grow to a final size that is influenced by the morphology of the microgel molecule, which thus acts as an exotemplate for the nanoclusters [10b].

Microgel-stabilized, size-controlled metal nanoclusters have recently found promising applications in different fields ranging from catalysis to drug delivery and materials science [10–15]. In particular, we have previously demonstrated the usefulness of Pd nanoclusters as catalysts in C–C coupling reactions, such as Heck and Suzuki couplings [10b,10c], as well as in the selective oxidation of secondary alcohols to the corresponding carbonyl compounds with molecular oxygen in water [10e]. In this contribution, we extend our investigation to microgel-stabilized Au nanoclusters and demonstrate their potential as catalysts for the aerobic oxidation of alcohols.

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. Preparation of microgel

Monomers were mixed in the molar ratio *N*,*N*-dimethylacrylamide:ethylene dimethacrylate:functional monomer 8:1:1 in a round-bottomed flask. The resulting mixtures (5 g) were diluted with cyclopentanone (45 g). Azobis(isobutyronitrile) (AIBN) (0.15 g, 3% w/w with respect to the monomer mixture) was then added. The resulting solution was degassed, put under nitrogen, and placed in a thermostatted oven preheated to 80 °C for 48 h. The polymerization solution was concentrated to about half of its original volume and subsequently poured into the fivefold volume of diethylether under efficient stirring. The precipitated solid was filtered off and dried under vacuum to constant weight. Isolated yields were >80% in all cases.

2.2. Preparation of microgel-stabilized Au nanoclusters

In the general procedure, 0.5 g of microgel was dissolved in dichloromethane (80 mL) under an inert atmosphere. $HAuCl_4$ (44 mg, 0.13 mmol) was then added, and the resulting solution was stirred at room temperature for 24 h. Subsequently, $NaHBEt_3$ (1.1 mL 1 M solution in THF) was added, and the resulting solution was stirred at room temperature for 1 day. The solution almost immediately changed in color from pale yellow to reddish-brown or reddish-purple, depending on the microgel used. The solution was concentrated to about half of its original volume, and the nanocluster-containing microgel was subsequently precipitated by pouring the solution into the fivefold volume of diethylether under efficient stirring. Isolated yields were about 90% in all cases.

2.3. Preparation of Au nanoclusters immobilized on active carbon

1% Au on AC catalyst was prepared as described previously with slight modifications [9b]. A polyvinyl-alcohol-stabilized sol was prepared by adding solid $NaAuCl_4 \cdot 2H_2O$ (0.043 mmol) and PVA (410 µL 2% w/w solution in water) to 130 mL of H_2O. After 3 min, $NaBH_4$ (1.3 mL 0.1 M solution in water) was added to the yellow solution under vigorous magnetic stirring. The brownish gold(0) sol was immediately formed. Within a few minutes of its generation, the colloid (acidified at pH 2, by sulphuric acid) was immobilized by adding activated carbon (X40S from Camel) under vigorous stirring. The amount of support was calculated to have a final metal loading of 1% w/w.

2.4. TEM measurements

Samples for TEM measurements were prepared by placing a drop of a solution of microgel-stabilized metal nanoclusters in dichloromethane or *N*,*N*-dimethylformamide on a carbon-coated copper grid, followed by solvent evaporation at room temperature. TEM micrographs were obtained at CIGS University of Modena, Italy, with a JEOL 2010 microscope with GIF operated 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 at atmospheric pressure

The catalytic tests were run in a three-necked, round-bottomed flask equipped with a reflux condenser and a gas inlet. In a typical procedure, a solution of microgel-stabilized metal nanoclusters (50 mg) in distilled water (4 mL) was placed into the flask, and 1-phenylethanol (0.13 mL, alcohol/metal ratio = 100 mol/mol) was then added. Then the apparatus was evacuated and flushed with dioxygen a couple of times, after which it was connected to a balloon filled with dioxygen. The reaction was started by placing the flask into an oil bath preheated to 100 °C and starting 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 ^{1}H NMR.

2.6. Catalytic tests under dioxygen pressure

The reactions were carried out in a thermostatted glass reactor (30 mL) provided with an electronically controlled magnetic stirrer and connected to a large reservoir (5000 mL) containing oxygen at 1.5 atm. The oxygen uptake was followed by a mass flow controller connected to a PC through an A/D board, plotting a flow/time diagram. Alcohol (0.3 M) and the catalyst (alcohol/metal = 500–3000 mol/mol) were mixed in distilled water (total volume 10 mL), containing 1 equivalent of NaOH. The reactor was pressurized at the desired pressure of O_2 (1.5–3 atm) and thermostatted at the appropriate temperature (50–70 °C). The reaction was initiated by stirring. In the case of partially soluble substrates, after the completion of the reaction, the catalyst was filtered off and the product mixture extracted with toluene. Catalyst recoveries were always $98 \pm 3\%$ with this procedure. In the case of homogeneous reactions, withdrawal of samples was carried out periodically.

Tests at controlled pH (glucose) were performed by setting the pH at 9.5 in a 718 STAT Titrino (Metrohom) equipped with a 0.3 M NaOH reservoir, pressurized at 3 atm of O_2. Glucose and the catalyst (substrate/metal = 3000 mol/mol) were mixed in distilled water (0.3 M). The temperature of the stirred mixture was kept at 50 °C, and as soon as the reaction started, a solution of 0.3 M NaOH was added automatically to maintain the pH of the solution at a fixed value (9.5 ± 0.1). The samples were analyzed at various times by high-pressure liquid chromatography (HPLC).

In the oxidation of 1-octanol, benzyl alcohol, and 1-phenylethanol, identification and analysis of products were carried out by gas chromatography using a Dani 86.10 HT gas chromatograph equipped with a capillary column (BP21, 30 m × 0.53 mm, 0.5 µm film thickness). Product identification was accomplished by comparison with authentic samples. The external calibration method was used to quantify the reagents and products.

In the oxidation of *n*-butanol, glycerol and glucose products were analyzed and quantified by means of HPLC on a Varian 9010 HPLC equipped with a Varian 9050 UV (210 nm) and a Waters RI detector in series. An Alltech OA-1000 column (300 mm × 6.5 mm) was used with aqueous H_3PO_4 0.1% w/w (0.5 mL/min) as the eluent. The procedures were as described previously [4,17].

3. Results and discussion

We previously reported on the preparation of microgel-stabilized Au nanoclusters using $AuCl_3$ as metal precursor and microgels prepared from *N*,*N*-dimethylacrylamide (DMAA) as the main comonomer, ethylene dimethacrylate (EDMA) as the cross-linker, and *N*,*N*-dimethylamino-ethylmethacrylate (DMAEMA) as the functional, metal-binding comonomer [10d,10e]. The microgels were loaded with gold(III) (5.5% Au) by letting their trialkylamino functional groups coordinate to $AuCl_3$ in water or ethanol. However, we found that the microgel-anchored gold(III) species prepared in this way underwent spontaneous reduction already in the course of the metal loading step. The actual reducing agents are probably the polymer-bound trialkylamino groups themselves, which are known to act in a similar way toward other, less easily reducible metal centers [18]. We ascribed to such an uncontrolled, spontaneous reduction the rather large size of the resulting Au nanoparticles (average diameter 10 ± 4 nm), which, as expected, exhibited poor activity in the aerobic oxidation of alcohols [10e]. Therefore, our initial aim was to overcome this problem by devising a way to control reduction of the gold precursors more precisely. First, we changed the nature of the gold(III) species and tried $HAuCl_4$. However, despite the fact that the spontaneous reduction process of microgel-bound $HAuCl_4$ was slower, it was still present. Therefore, we changed the nature of the functional monomer in the microgels, choosing to use the functional monomers methylthio-ethylmethacrylate (MTEMA) or vinylpyridine (VP) instead of DMAEMA. Microgels containing the two novel functional monomers could be prepared without deviating from the already-used synthetic procedure. The molar composition of the monomer mixture was DMAA:EDMA:functional monomer 8:1:1 in all cases; the polymerization conditions were as reported in Section 2. The microgels could be conveniently isolated by precipitation as white powders that were readily redispersible in water and in many different organic solvents, including alcohols, dialkylamides, nitriles, dichloromethane, acetone, and THF.

Microgel loading could be conveniently performed with $HAuCl_4$ in dichloromethane. The resulting solutions remained golden yellow for hours with no observable color change, indicating no metal reduction to Au nanoparticles. In contrast, an almost instant color change to the characteristic reddish color of Au nanoclusters occurred when $NaHBEt_3$ was added to the microgel solution.

TEM analyses were performed to assess the size of the microgel-stabilized metal nanoclusters. Microgels based on MTEMA as the nonfunctional monomer yielded Au nanoclusters with an average size of 5.2 ± 1.4 nm, whereas microgels based on VP favored the formation of much smaller nanoclusters (2.4 ± 0.7 nm) with a narrow size distribution (Fig. 1). These results confirm our previous observation that a more controlled reduction of the microgel-bound metal precursors lead to smaller metal nanoclusters with a narrower size distribution. On the other hand, these results also point out that the functional monomer may have a significant influence on the final size of gold nanoclusters. We are currently investigating this aspect in more detail.

The dichloromethane solutions of microgel-stabilized Au nanoclusters prepared as outlined above were clear and stable. The nanocluster-containing microgels could be conveniently isolated by precipitation and stored as powders. The powders thus obtained could be readily redispersed in polar solvents such as water, alcohols, or dialkylamides; in contrast, on storage in the dry state, they quickly became largely insoluble in less polar organic solvents, including dichloromethane (i.e., the solvent in which they were prepared). We are currently attempting to rationalize this aging phenomenon.

As mentioned earlier, these microgels could be conveniently used in solution for catalytic purposes. The advantage of using dispersed nanoclusters instead of classical supported nanoclusters lies in the higher exposed surface of the metal and also in the resulting "quasi-homogeneous" system, which prevents diffusional limitations.

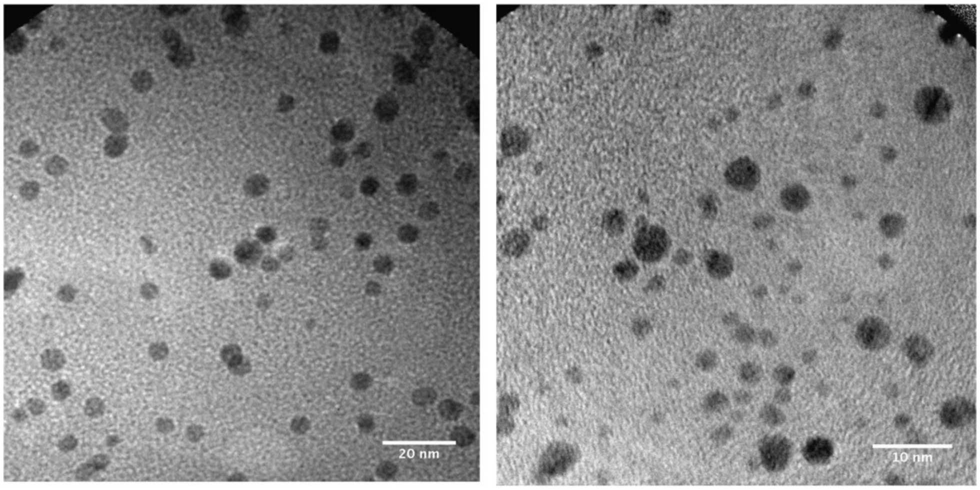

Fig. 1. TEM micrographs of Au nanoclusters stabilized by microgels based on MTEMA (left) and VP (right).

The catalytic tests were initially run under the reaction conditions originally proposed by Uozumi and Nakao for Pd metal catalysts [19] (water, neutral pH, 100 °C, 1 atm O_2, 1 mol% metal) with 1-phenylethanol as standard substrate. We previously successfully used these conditions with other microgel-stabilized metal nanocluster catalysts [10e]. Au nanoclusters protected by microgels based on the MTEMA monomer were completely inactive as catalysts. Considering the high affinity of gold for sulfur-containing compounds, it seems that the amount of thioether groups present in the microgel is sufficient to completely deactivate the surface of the gold nanoclusters for the reaction. It must be noted, however, that gold nanoclusters supported on insoluble functional resins bearing the same thioether groups in lower concentration are active catalysts for this kind of reaction [20]. On the other hand, Au nanoclusters protected by microgels based on the VP monomer were very active for the reaction, yielding the product in 100% yield after 24 h of reaction (not optimized). This catalytic efficiency appears to be somewhat lower than that of microgel-stabilized Pd nanoclusters of similar size, where complete conversion was reached within 6 h under identical reaction conditions [10e], but we note that such a result was obtained at *neutral* pH. In fact, gold metal catalysts usually require a basic pH to display activity for the aerobic oxidation of alcohols in water [7,21], although it was recently demonstrated that the oxidation of benzyl alcohol can be carried out with gold metal catalysts under solvent-less, base-free conditions [22].

We set out to evaluate the reactivity of our catalyst at basic pH, but unfortunately our attempts were frustrated by catalyst precipitation in the course of the reaction, which invariably occurred above ca. 80 °C. At present, it is unclear whether precipitation must be ascribed to microgel decomposition and/or nanoparticle aggregation, or else to a thermomorphic behavior of the microgel; such a behavior actually has been already observed with Pd nanoclusters stabilized by the same microgel [23].

Therefore, we chose to change the reaction conditions, and adopted those routinely used by Prati et al. with supported Au colloids (1/500 to 1/3000 metal/substrate molar ratio, 50–70 °C, 1–3 atm O_2). Using these reaction conditions also allowed a meaningful comparison with other previously tested gold-based catalysts.

Table 1
Oxidation of alcohols with dioxygen in water catalyzed by microgel-stabilized Au nanoclusters or 1% Au-AC

Alcohol	Time (h)	Catalyst	Conversion (%)	TOF (h^{-1})	Selectivity (%)
1-Phenylethanol	1	Microgel	75	375	100 (ketone)
	1	1% Au-AC	61	305	100 (ketone)
Benzyl alcohol	0.25	Microgel	48	960	49 (aldehyde); 36 (acid)
	0.25	1% Au-AC	57	1140	32 (aldehyde); 41 (acid)
1-Octanol	4	Microgel	59	74	84 (acid)
	4	1% Au-AC	24	30	77 (acid)
	8		65		93 (acid)
n-Butanol[a]	2	Microgel	56	280	88 (acid)
	4		76		100 (acid)
	2	1% Au-AC	32	160	81 (acid)
	4		54		89 (acid)

Note. Reaction conditions: 0.3 M alcohol, 0.3 M NaOH, 1.5 atm O_2, 60 °C, 1/500 metal/substrate (mol/mol).

[a] Reaction performed at 3 atm O_2, 70 °C, 1/1000 metal/substrate (mol/mol).

First, we verified that by using temperatures in the range 50–70 °C, no precipitation of Au-VP microgel was observed even using a strongly basic additive (NaOH). Subsequently, we ran the catalytic tests using as substrates *n*-butanol, *n*-octanol, benzyl alcohol, 1-phenylethanol, and also glycerol and glucose to investigate the chemoselectivity of the reaction. The results are shown in Tables 1 and 2, where data obtained by using gold nanoparticles of similar dimension (3–4 nm) but supported on activated carbon (1% Au-AC) are also reported for comparison.

Microgel-stabilized Au nanoclusters showed in general good activity with simple alcohols and, apart from the case of benzyl alcohol, behaved slightly better than carbon-supported nanoclusters of almost the same size. The recorded catalytic activity was remarkable with all substrates, reaching, as expected, its

Table 2
Oxidation of glycerol and glucose with dioxygen in water catalyzed by microgel-stabilized Au nanoclusters or 1% Au-AC

Substrate	Time (h)	Catalyst	Conversion (%)	Selectivity (%)		
				Glycerate	Glycolate	Tartronate
Glycerol[a]	0.25	Microgel	10	47[b]	48	1
	0.5		15	50[b]	46	1
	1		29	52[b]	46	1
	0.25	1% Au-AC	26	60[b]	26	7
	0.5		55	60[b]	26	8
	1		83	61[b]	23	11
Glucose[c]	0.5	Microgel	6	>99[d]		
	1		15	>99[d]		
	4		35	>99[d]		
	0.25	1% Au-AC	28	>99[d]		
	0.5		56	>99[d]		
	1		81	>99[d]		

[a] Reaction conditions: 0.3 M glycerol, 1.2 M NaOH, 3 atm O_2, 50 °C, 1/1000 metal/substrate (mol/mol).

[b] Selectivity to glycerate.

[c] Reaction conditions: 0.3 M glucose, 3 atm O_2, 50 °C, 1/3000 metal/substrate (mol/mol), maintaining pH at 9.5 by adding 0.3 M NaOH.

[d] Selectivity to gluconate.

maximum with activated alcohols, such as benzyl alcohol and 1-phenylethanol.

The reaction gave full selectivity for ketone in the case of secondary alcohols, whereas with primary alcohols (and especially with aliphatic alcohols), the carboxylic acid was formed, sometimes together with a limited amount of the corresponding ester. This tendency toward further oxidation of the intermediate aldehyde was also expected, because it is well known that aldehydes are hydrated in water and in this form are oxidized by gold metal catalysts more efficiently than the starting alcohol [1].

The obtained activities compare favorably with most other reported catalytic systems based on Au metal nanoparticles. Hutchings's Au/TiO_2 or Au/zeolite catalysts yielded at low conversion with benzyl alcohol a $\mathrm{TOF}_{t=0.5\,\mathrm{h}}$ of 200–500 h^{-1} at 100 °C and 2 atm O_2 under solvent-less conditions [22]. Baiker's catalyst (Au on Cu–Mg–Al mixed oxides) gave at 90 °C and 1 atm O_2 in mesitylene a $\mathrm{TOF}_{t=0.5\,\mathrm{h}}$ of 316 h^{-1} with benzyl alcohol and a $\mathrm{TOF}_{t=3\,\mathrm{h}}$ of 11 h^{-1} with 1-octanol; much better results were obtained with 1-phenylethanol ($\mathrm{TOF}_{t=1\,\mathrm{h}}$ of 1294 h^{-1}) [24]. Oxidation of 1-phenylethanol with Kobayashi's Au on polystyrene gave a $\mathrm{TOF}_{t=1\,\mathrm{h}}$ of 32 h^{-1} at room temperature and 1 atm O_2 in benzotrifluoride:water 1:1 [25]. Oxidation of 4-hydroxybenzyl alcohol using Tsukuba's PVP-stabilized Au nanoclusters in water gave an actual $\mathrm{TOF}_{t=1\,\mathrm{h}}$ at 23 °C and 1 atm O_2 of 15 h^{-1} and an estimated $\mathrm{TOF}_{t=1\,\mathrm{h}}$ at 60 °C and 1.5 atm O_2 of 33 h^{-1} [4b,7]. Finally, Corma's Au on nanocrystalline CeO_2 with benzylic alcohols exhibited a $\mathrm{TOF}_{t=2\,\mathrm{h}}$ of about 80 h^{-1} at 50 °C and 1 atm O_2 in water [26], although in this case alcohol oxidation actually was carried out by the cerium(IV) centers in the support, with the Au metal merely acting to regenerate these centers with concomitant O_2 reduction.

When aliphatic alcohols were used, the beneficial effect of using gold nanoclusters in microgel-stabilized, quasi-homogeneous form instead of having them heterogenized on carbon was more apparent. The activity of the Au-VP catalyst was ca. twice that of Au-AC, whereas selectivities at isoconversion were comparable. Moreover, apparently the more oxidizable the substrate becomes, the more 1% Au-AC becomes active with respect to Au-microgel; indeed, the difference in activity between the two catalysts decreases in the order *n*-octanol > *n*-butanol > 1-phenylethanol > benzyl alcohol, with 1% Au-AC being more active than Au-microgel in the latter case.

Using multifunctionalized substrates, such as glycerol or glucose, we instead observed that 1% Au-AC was always more active than Au-microgel, as shown in Table 2. We also observed a difference in selectivity between Au-microgel and Au/C, with former being more prone to C–C bond scission than the latter. Thus, it seems that the catalyst activity also could be related to the hydrophobicity or hydrophilicity of the substrate. In fact, partial agglomeration of catalyst and substrate was observed when *n*-octanol was used as the substrate and Au-AC as the catalyst [27]. This behavior can be clearly ascribed to the hydrophobic nature of the carbon surface, which could be wetted by octanol more readily than by water. Incidentally, catalyst agglomeration, as well as preferential absorption of the reagent, limit the accessibility of the catalyst surface by the water phase in which the second reactant (O_2) is dissolved, thereby limiting the reaction rate. This limiting step was not observed using Au-microgel that was rapidly dissolved in the aqueous medium. In this case, 1-octanol was dispersed into the solution by stirring. When more hydrophilic substrates were used instead, a "normal" triphasic system was obtained, and access to the active surface was not limited by an organic layer even in the case of Au-AC.

4. Conclusion

In the present work, we have demonstrated the possibility of extending our method for the preparation of microgel-stabilized, size-controlled metal nanoclusters to Au nanoparticles. Through proper choice of the functional monomer in the microgel (vinylpyridine), Au nanoclusters of small size and with a narrow size distribution can be generated. The resulting microgel-stabilized Au nanoclusters have been shown to be remarkably active "quasi-homogeneous" catalysts for the aerobic oxidation of primary and secondary alcohols in water. From a catalytic standpoint, we note that the exposed surface plays a determining role, and also that the relative affinity of the substrate and the support for aqueous media should be taken into account in forecasting the catalytic activity of gold particles in liquid-phase oxidation.

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