Metal nanoclusters stabilized by pH-responsive microgels: Preparation and evaluation of their catalytic potential[☆]

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ABSTRACT

Unstabilized, pH-responsive soluble crosslinked polymers (microgels) bearing pendant trialkylamino or pyridyl groups and containing size-controlled Au or Pd nanoclusters have been prepared by radical copolymerization in dilute solution, followed by loading with $HAuCl_4$ or $Pd(OAc)_2$ and chemical reduction. The hydrodynamic volume, the solubility and the partition between immiscible solvents of the microgels and of the resulting microgel-metal nanocomposites have been investigated, together with the variation of these parameters with the solution pH: separation of our microgel-containing metal nanoclusters from aqueous solutions can be accomplished by precipitation or by extraction into an organic solvent phase upon pH change, thus enabling their potential recovery. The catalytic performance of the microgels in the aerobic oxidation of benzyl alcohol (Au) and in Sonogashira coupling reactions (Pd) has been determined. The microgel-Au nanocomposites exhibit poor catalytic activity, whereas better results have been obtained in the copper-free Sonogashira reaction with microgel-Pd nanocomposites as precatalysts.

1. Introduction

Stimuli-responsive, soluble crosslinked polymers (microgels) are at present the subject of intense research, with applications encompassing various fields of chemistry, most notably drug delivery, sensing, and catalysis [1,2]. Concerning in particular the catalysis field, their responsiveness has been put to advantage for triggering and controlling the performance of catalysts located within the microgel through swelling/deswelling of the microgel network [3]. In the vast majority of cases, temperature-responsive microgels have been employed for this purpose [3,4], whereas much less work has been conducted on pH-responsive systems; indeed, although for example pH-responsive microgels containing metal nanoparticles have been synthesized and their usefulness for several purposes, including catalysis, has been predicted [5], only very few examples of exploitation of such a pH-responsiveness to control the performance of the nanoparticles have appeared in the literature up to now [6]; in most of these instances, pH-responsiveness was employed to control the spectroscopic properties of the metal nanoparticles (surface plasmon resonance, fluorescence) and only in one case an effect of pH on the catalytic properties was unambiguously determined [6d]. Remarkably, apart from enabling control of catalytic

efficiency through swelling/deswelling, as well as straightforward catalyst separation and recycling upon precipitation or liquid-liquid extraction [7], the presence of pH-sensitive (acid or basic) groups in the microgel may also serve to promote the catalytic event taking place within the microgel network through a proximity effect of such groups to the catalytically active center [8], a possibility yet to be investigated in detail.

We have a longstanding interest in the preparation, characterization and application of functional microgels [9]; in particular, our group was the first to investigate on the application of microgel-stabilized metal nanoclusters as catalysts [10]. In the present contribution, we report on our results concerning the preparation of pH-responsive microgels bearing pendant basic (trialkylamino, pyridyl) groups, on their use as exotemplates in the preparation of size-controlled Au and Pd nanoclusters and on the application thereof as catalysts for technologically relevant reactions such as aerobic alcohol oxidations and copper-free Sonogashira coupling reactions.

2. Experimental section

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 prior to use. DLS analyses were carried out with a Malvern Zetasizer Nano instrument. TEM analyses were carried out with a JEM 3010 (JEOL) electron microscope operating at 300 kV, point-to-point resolution at a Scherzer defocus of 0.17 nm. GC analyses were performed with a Dani 86.10 HT Gas Chromatograph equipped with a capillary column BP21, 30 m × 0.53 mm, 0.5 μm film thickness made by SGE. NMR analyses were run on a Bruker Avance spectrometer working at 300 MHz. ICP-AAS measurements were performed on an Ametek Spectro Genesis instrument.

2.1. Microgel preparation

2.1.1. General procedure

Monomers were mixed in the molar ratio functional basic monomer:ethylene dimethacrylate 9:1 or functional basic monomer:N,N-dimethylacrylamide:ethylene dimethacrylate 5:4:1 in a round-bottomed flask. The resulting mixture (5 g) was 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 argon and placed for 20 h in a thermostated oven preheated at 80 °C. The polymerization solution was concentrated to about half of its original volume and subsequently poured into the fivefold volume of petroleum ether under efficient stirring. The precipitated solid was filtered off and dried under vacuum to constant weight. Compositions and isolated yields of the various microgels are reported in Table 1.

2.2. DLS measurements

Microgel solutions for DLS measurements were prepared by dissolving 100 mg microgel into 100 mL water acidified below pH 4 with HCl 0.1 M. The pH of the solution was subsequently adjusted at pH 2, 4, 6 and 8 by addition of 0.1 M NaOH/0.1 M HCl; the actual pH value was checked with a pH-meter. The results of the measurements are reported in Table 2.

2.3. Preparation of microgel-stabilized Au nanoclusters

2.3.1. General procedure

Microgel (0.250 g) was dissolved in dichloromethane/acetonitrile (20 + 20 mL). $HAuCl_4$ (5.1 or 25.5 mg) was then added, and the resulting solution was stirred at room temperature for 4 h. Subsequently, $NaHBEt_3$ (1.1 mL 1 M solution in THF) was added and the resulting solution was stirred at room temperature overnight. The solution almost immediately changed its colour from pale yellow to reddish-purple. 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 diethyl ether under efficient stirring to yield a dark purple powder. Isolated yields of the various microgel-Au nanocomposites are reported in Table 3.

Table 1
Isolated microgel samples.

Sample	mol% basic comonomer	mol% DMAA	mol% EDMA	Yield (%)
DMA90	90 (DMAEMA)	0	10	88%
DEA90	90 (DEAEMA)	0	10	83%
2VP90	90 (2-VP)	0	10	98%
4VP90	90 (4-VP)	0	10	78%
DMA50	50 (DMAEMA)	40	10	98%
DEA50	50 (DEAEMA)	40	10	73%
2VP50	50 (2-VP)	40	10	58%
4VP50	50 (4-VP)	40	10	61%

Table 2
DLS data (average hydrodynamic radius, nm) of the microgels in water at different pH.

Sample	pH = 2	pH = 4	pH = 6	pH = 8
DMA90	82	99	249	Flocculation
DEA90	101	108	123	> 1000
2VP90	167	161	Flocculation	Flocculation
4VP90	59	126	> 1000	Flocculation
DMA50	57	48	113	97
2VP50	452	> 1000	Flocculation	Flocculation

Table 3
Isolated microgel nanocomposite samples.

Microgel nanocomposite[a]	Yield (%)	Microgel nanocomposite[a]	Yield (%)
DMA90-1Au	96	DMA50- 5Au	76
DEA90-1Au	55	DEA50-5Au	97
2VP90-1Au	96	2VP50-5Au	96
4VP90-1Au	98	4VP50-5Au	73
DMA50-1Au	31	DMA90-1Pd	93
DEA50-1Au	22	DEA90-1Pd	30
2VP50-1Au	80	2VP90-1Pd	95
4VP50-1Au	98	4VP90-1Pd	98
DMA90-5Au	68	DMA50-1Pd	95
DEA90-5Au	43	DEA50-1Pd	80
2VP90-5Au	99	2VP50-1Pd	97
4VP90-5Au	98	4VP50-1Pd	99

[a] The number before the metal symbol indicates the nominal metal content (% by weight) in the nanocomposite.

2.4. Preparation of microgel-stabilized Pd nanoclusters

2.4.1. General procedure

Microgel (0.500 g) was dissolved in dichloromethane (20 mL). Pd(OAc)$_2$ (10.5 mg) was then added, and the resulting solution was stirred at room temperature for 4 h. Subsequently, $NaHBEt_3$ (1.1 mL 1 M solution in THF) was added and the resulting solution was stirred at room temperature overnight. The solution almost immediately changed its colour from orange yellow to greyish brown. 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 petroleum ether under efficient stirring to yield a greyish brown powder. Isolated yields of the various microgel-Pd nanocomposites are reported in Table 3.

2.5. TEM measurements

Microgel samples for TEM measurements were prepared by placing a drop of a solution of microgel-stabilized metal nanoclusters in ethanol on a carbon-coated copper grid followed by solvent evaporation at room temperature. Average metal nanocluster sizes and size distributions were computed as the average of at least 100 particles taken from different fields.

2.6. Catalytic tests: aerobic alcohol oxidation

The reactions were carried out in a thermostated glass reactor (30 mL) provided with an electronically controlled magnetic stirrer and connected to a large reservoir (5000 mL) containing dioxygen at 2.0 atm. The dioxygen uptake was followed by a mass flow controller connected to a PC through an A/D board, plotting a flow/time diagram. For the tests in water, benzyl alcohol (0.3 M) and the catalyst (alcohol/gold = 1000 mol/mol) were dissolved in distilled water (total volume 10 mL), whereas for the tests under neat conditions the catalyst was directly dissolved into benzyl alcohol (alcohol/gold = 5000 mol/mol). The reactor was pressurised at 2 atm O$_2$ and thermostated at 80 °C. The reaction was initiated by stirring and monitored by periodically with-