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Letter

Functionalised microgels: novel stabilisers for catalytically active metal colloids

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Abstract

Microgel stabilised palladium colloids have been prepared by a novel strategy based on the synthesis of microgels upon radical solution copolymerisation of suitable functional monomers containing sulfonic acid groups. These microgels can be conveniently loaded with Pd^{2+} ions which are subsequently reduced. The resulting metal colloids (10–20 nm diameter) can be precipitated from the reaction mixture and redispersed in suitable solvents. Preliminary tests indicate that microgel stabilised palladium colloids are active catalysts for the vinylation of aryl iodides and bromides (Heck reaction). © 2001 Elsevier Science B.V. All rights reserved.

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In polymer chemistry, the term "microgel" [1] defines unimolecular, crosslinked polymer particles possessing a size comparable to the statistical dimensions of uncrosslinked macromolecules (10^1–10^2 nm), which can give raise to stable solutions in appropriate solvents. These materials, first described by Staudinger [2] in the 1930s, can be considered as an intermediate category of polymers which combine the characteristics of both linear macromolecules and three-dimensional networks. For a comprehensive review on microgels, see [3].

Microgels have found wide technological application as additives with binding or stabilising properties in the industrial manufacture of coatings [4]. Furthermore, in recent years, the recognition of their unique characteristics has stimulated considerable research on their use as controlled release devices [5], phase transfer catalysts [6] and as soluble supports for low molecular weight reagents and catalysts [7–11]. The latter application appears particularly appealing, in that the use of microgels offers the possibility to overcome the serious drawbacks usually associated with the unavoidably restrained transport properties inside conventional insoluble catalyst supports. A microgel supported catalyst behaves in fact as a *homogeneous* catalyst which, however, can be conveniently separated from the reaction mixture by means of precipitation, ultracentrifugation or ultrafiltration. Moreover, thanks to their globular nature microgels do not pose the handling problems often encountered with highly viscous solutions of functionalised linear polymers. Finally, microgels can be analysed by standard techniques available for soluble macromoleules, which relieve the problems associated with the

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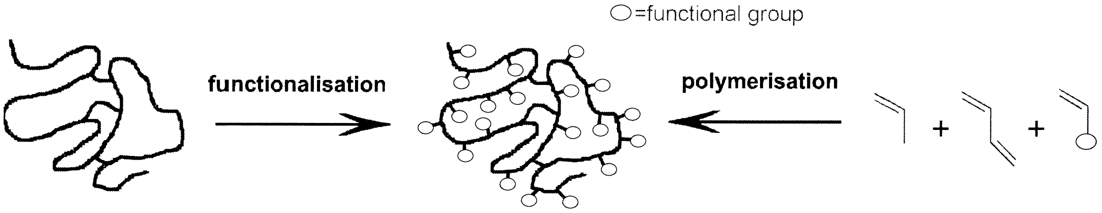


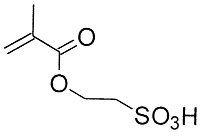
Fig. 1. Possible strategies for the synthesis of functionalised microgels: functionalisation of preformed microgels (left) or copolymerisation of suitable functional monomers (right, our approach).

characterisation of an insoluble material such as a conventional support.

Among the reactive species which can be supported on (and stabilised by) microgels, metal nanoclusters and colloids appear particularly interesting. Indeed, there is a large potential for the application of readily processable, size controlled metal nanoparticles in catalysis [12] as well as in the field of material science [13].

The first report on the preparation of microgel stabilised metal colloids was published in 1997 by Antonietti et al. [14], who utilised polystyrene based microgels prepared by microemulsion polymerisation and fully sulfonated in a second step by treatment with concentrated sulfuric acid. The sulfonated microgels were soluble in water and could be conveniently loaded with gold ions, which were subsequently reduced, thus, forming the microgel stabilised colloids. To the best of our knowledge, this is the only example of the preparation of microgel stabilised metal colloids published to date. We wish to report on the use of sulfonated microgels prepared by an alternative route, namely by copolymerisation of suitable functional monomers (Fig. 1).

This methodology presents some fundamental advantages. First, it represents a much milder method for the introduction of the sulfonic acid groups, which is not limited by the nature of the polymer backbone. Secondly, our method enables to easily control the amount of sulfonic groups in the microgels, hence, the hydrophilic/hydrophobic properties of the microgel support. As a consequence, it is possible to prepare microgel stabilised metal colloids which are soluble in organic solvents. Finally, our method is evidently not limited to the synthesis of microgels functionalised with sulfonic groups. In fact, alternative acidic functionalities (e.g. carboxylic acid groups) as well as basic or metal coordinating groups can be incorporated into the microgel backbone simply upon utilisation of suitable functional comonomers. It is important to remark that this strategy for the synthesis of microgel stabilised colloids appears to be very general: such colloids can potentially be prepared from every metal containing precursor suitable to be anchored to microgel bound functional groups and subsequently to be reduced to the metal state.



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Radical polymerisation in dilute solution was used throughout this work for microgel synthesis [2,15]. This is probably the simplest available method for the preparation of microgels. It does not make use of surfactants or other additives; it only needs a careful choice of the reaction parameters, most notably of the nature of the solvent, in order to avoid gelation and maximise the microgel yield. In comparison to the more common preparation method by polymerisation in microemulsion, solution polymerisation suffers from a less precise control of the size and size distribution of the resulting microgels. On the other hand, the polymerisation in solution offers the considerable advantage of allowing the variation of parameters, such as the type and degree of microgel functionalisation (by utilising suitable comonomers), the nature of the nonfunctional comonomers or the crosslinking degree,

Table 1
Monomer mixtures employed in the preparation of functionalised microgels[a]

Microgel	MMA (% w/w)	EDMA (% w/w)	**1** (% w/w)	Solvent
M1	60	20	20	DMF
M2	75	5	20	EtOH
M3	70	10	20	EtOH
M4	60	20	20	EtOH
M5	50	30	20	EtOH

[a] Polymerisation conditions: 3% w/w AIBN, 5% w/w concentration of monomers in the solvent of choice, 80°C, 4 days.

with less restrictions caused by the requirements of the polymerisation procedure. These parameters play an important role in determining the solubility of the microgels in different solvents and possibly the dimensions of the metal colloids resulting from the ion exchange and reduction procedure.

Upon using sulfonated monomers such as the sulfoethylmetacrylate **1** microgels were prepared utilising methyl metacrylate (MMA) and ethylene dimetacrylate (EDMA) as the comonomers, with a crosslinking degree up to 30% w/w (Table 1). The amount of sulfonated monomer was chosen in order to provide a content of sulfonic groups in the microgel equal to 1 meq./g. The microgels could be conveniently precipitated from the polymerisation solutions by pouring them in suitable nonsolvents such as hexane or diethylether. The microgels separated as white powders, readily redispersable in good solvents such as dialkylamides, ethanol and acetonitrile.

Ion-exchange with palladium acetate was performed in acetonitrile. $Pd(OAc)_2$, 0.25 moles per mole of sulfonic groups was added to a microgel solution in acetonitrile under an inert atmosphere. The initially orange solutions became gradually darker as a consequence of the partial reduction of the microgel bound Pd^{2+}-sulfonate species formed upon protonation of the acetate ligands. The apparent limited redox stability of polymer-bound Pd^{2+}-sulfonate species inside insoluble functional resins was recently observed in these laboratories [16]. The metal reduction was completed by adding ethanol and refluxing the resulting solution for 24 h. This procedure led to the formation of microgel stabilised Pd colloids which could be conveniently isolated from the reaction solution by pouring it in excess diethylether. The obtained dark-grey powders were still readily redispersable in suitable mediums such as ethanol, acetonitrile, dimethylformamide or dimethylacetamide. The resulting colloidal suspensions were clear and turned out to be stable for months without any observable precipitation of Pd black.

The size and size distribution of the microgel stabilised Pd colloids produced in this way were investigated by TEM. A TEM micrograph of a sample of microgel stabilised colloids M1-Pd is reported in Fig. 2. It can be seen that the size distribution of the metal particles is rather broad and that the particle size lies in the 10–20 nm range. The reason for the attainment of such relatively large particle sizes and broad size distribution is probably related to the instability of the microgel-bound Pd^{2+}-sulfonate species, which causes the uncontrolled reduction to the metal, and possibly also to the reductant utilised to complete the reaction (ethanol). We are currently trying to gain more control over this step by (1) utilising microgel bound functional groups which give stable complexes with palladium(II) species like, e.g. nitrogen bases, and (2) performing the reduction step with a faster reductant, like e.g. $NaBH_4$, in order to produce particle sizes in the 3–5 nm range, which is typical for Pd colloids generated by similar methods inside insoluble functional resins [17].

The microgel-stabilised Pd colloids were tested as catalysts in the Heck reaction of aryl halides with *n*-butylacrylate using sodium acetate as the base. Preliminary results obtained with catalyst M1-Pd indicate that these materials are active catalysts for this reaction. To the best of our knowledge, this is the first example of a reaction catalysed by microgel stabilised metal colloids. The results are reported in Table 2.

High yields in Heck coupling products are obtained with iodobenzene and with activated aryl bromides such as 4-bromoacetophenone. On the contrary, no reaction is observed with bromobenzene whereas only a poor yield is obtained with activated aryl chlorides such as 4-chloroacetophenone. Remarkably, the suspension of the microgel-stabilised colloidal catalyst appears to be stable in all cases under the relatively severe reaction conditions employed and no precipitation of Pd black is observed. In comparison to the results previously obtained by other groups with

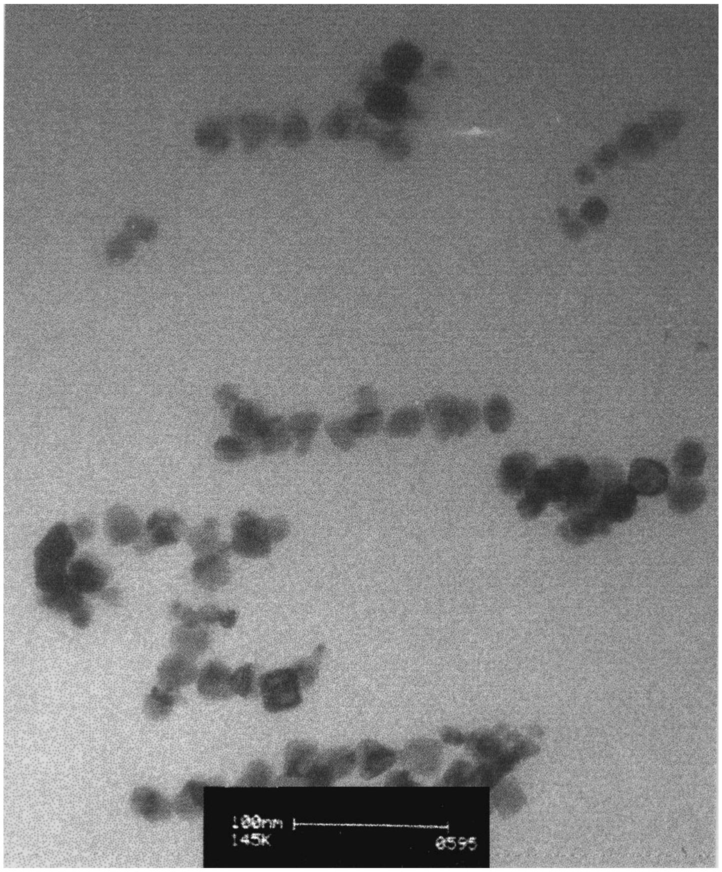

Fig. 2. TEM micrograph of Pd nanoparticles stabilised by microgel M1.

colloidal suspensions of palladium stabilised by different means [18–20], the catalytic activity of the investigated colloids appears somewhat lower. However, the literature data were often obtained under significantly different reaction conditions (higher reaction temperature and/or higher amount of catalyst). The observed lower activity could be a consequence of the relatively large particle size of the colloids employed in this work. We wish to stress that the yields listed above are not optimised and can expectedly be improved by adjusting parameters such as the reaction temperature and the nature of the employed base.

In conclusion, we have shown that remarkably stable microgel stabilised palladium colloids can be prepared by simple means starting from suitably functionalised microgels. Moreover, we have shown that such colloids are active catalysts for the Heck reaction. Further work is in progress in order to increase the control over the metal particle size and size distribution and to extend this kind of chemistry to other metals and other catalytic reactions.

Table 2
Heck reaction using microgel-stabilised catalyst M1-Pd[a]

Aryl halide	Reaction yield (%)
Iodobenzene	75
4-Bromoacetophenone	65
Bromobenzene	0
4-Chloroacetophenone	6

[a] Reaction conditions: 10 mmol aryl halide, 10 mmol NaOAc, 17 mmol *n*-butylacrylate, 83 mg catalyst (0.2% m/m), 25 ml *N*,*N*-dimethylacetamide; inert atmosphere (N_2), 120°C, 24 h. Selectivity for the Heck product was 100% in all the cases.

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