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Metal nanoparticles inside microgel/clay nanohybrids: Synthesis, characterization and catalytic efficiency in cross-coupling reactions

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ABSTRACT

Hypothesis: Laponite nanoclay embedded inside soluble crosslinked copolymers (microgels) may act as cation exchanger allowing loading of the microgels with cationic metal precursors, which upon reduction yield tailored ternary colloidal nanocomposites comprising both nanoclay and metal nanoparticles.
Experiments: Microgel nanohybrids with variable Laponite nanoclay content were loaded with cationic precursors of different noble metals (Pd, Pt, Au); subsequent reduction by several methods yielded ternary nanocomposites which were extensively characterized. Nanocomposites based on Pd were also tested as catalysts in standard Suzuki and Sonogashira cross-coupling reactions.
Findings: The proposed method for the production of ternary nanocomposite microgels has been validated. The factors influencing the final metal nanoparticle size (nature of the reducing agent, clay content in the microgel) have been determined and rationalized. The resulting Pd-containing ternary nanocomposite microgels are viable catalysts of standard cross coupling reactions in water-rich medium.

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1. Introduction

Sub-micrometer sized, crosslinked polymer colloids (microgels) are a class of nanomaterials featured by attractive properties (defined size, tailored morphology and porosity, variable nature and degree of chemical functionality, low viscosity, film forming ability) which find application in widely different areas ranging from coatings to medicine, from molecular recognition to catalysis [1,2]. In recent years, fundamental as well as applied research on microgels has been extended to nanosystems containing a second component embedded in the microgel structure, which can be organic (proteins, polymers) or inorganic (metals, metal oxides, metal sulfides) in nature [3]. The preparation of such nanocomposites ensures on the one hand an enhancement of the compatibility between the two components, which is useful for example in the manufacture of cosmetics, inks and paints (enhancement of compatibility between filler and binder). On the other hand, these nanomaterials offer the opportunity to combine the properties of microgels with those of the incorporated component (e.g. luminescence, magnetism, catalytic activity), thereupon yielding multifunctional colloids with numerous potential technological applications. Examples of this concept have been recently described, particularly upon combining stimuli-responsive microgels with metal nanoparticles: the resulting nanomaterials have been employed as catalysts featured by switchable activity/separability [3c] or as infrared-responsive controlled release devices [4].

Several groups, including ourselves, have reported in the past on the generation, characterization and application of metal nanoparticles inside microgels [5]; in particular, some of us were the first to highlight the exotemplating effect of the microgel in these syntheses, leading to the formation of metal nanoparticles of predetermined size which depends on the morphological features of the microgel network [5b,6]. Furthermore, in recent times some of us, as well as others, have investigated on the preparation of composite microgels based on clays and have demonstrated their usefulness as e.g. responsive scavenger systems [7]. Clays have cation-exchange capacities, hence their incorporation into microgels turns into a mean for charging the resulting composite nanoparticles with (cationic) metal precursors, which upon reduction generate metal nanoparticles inside the microgel/clay nanocomposites; the presence of clay in the microgels may also contribute to the stabilization of the resulting metal nanoparticles (due to their adsorption on clay), thereby helping to avoid leaching as well as clustering of the metal nanoparticles under catalytically relevant

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conditions. The evaluation of such a synthetic strategy as well as the catalytic application of the resulting ternary nanocomposites (microgel/nanoclay/metal nanoparticles) forms the object of this work.

2. Results and discussion

2.1. Synthesis

The microgel/clay nanohybrids were prepared as previously described using as clay component Laponite nanoparticles dispersed in the polymerization mixture during formation of poly(N-vinylc-aprolactam-co-acetoacetoxyethyl methacrylate) (PVCL/AAEM) microgel particles by precipitation polymerization [7c]. Microgel nanohybrids with a clay content ranging from 5% to 15% by weight were used for this work. In order to load the nanohybrids with metal precursors, stable cationic precursors in aqueous solution had to be chosen, since we envisaged exploiting the cation-exchange capabilities of the clay component. Thus, commercially available or easily synthesizable cationic complexes of noble metals featured by good solution stability were employed for this work, such as $[Pd[(NH_3)_4](NO_3)_2$, $[Pt(NH_3)_2Cl_2]$, $[Au(en)_2]Cl_3$ (en = ethylenedia mine).

The loading procedure was accomplished by simply dissolving in a water dispersion of the microgel/clay nanohybrid an amount of the metal precursor sufficient to reach a nominal content of 1–10% by weight of metal in the dry microgel. The resulting dispersions were stirred overnight, in which time the ion-exchange took place, as subsequently confirmed by extensively washing the solution with water in an ultrafiltration stirring cell and determining the amount of residual metal in the filtrate by ICP–AAS. The metal precursors anchored to the microgels were then reduced to metal nanoparticles using different reducing agents, namely NaBH₄, ethanol, or dihydrogen.

Use of NaBH₄ was possible only for the microgels with the lowest metal content, since in the other cases the amount of added reducing agent (which is usually employed in excess with respect to the metal) increased the ionic strength of the solution to the point that the colloidal stability of the microgel was hampered and flocculation was observed. This procedure resulted in the preparation of a series of nanocomposites differing upon clay content, nature of the metal component, amount of metal, and nature of the reducing agent. The synthesized nanocomposites are summarized in Table 1.

2.2. Characterization

The ternary microgel nancomposites were extensively characterized by TEM analysis of the metal nanoparticles and by Dynamic

Light Scattering (DLS). The results are reported in Table 2. Analysis of the TEM micrographs of the various samples invariably showed monomodal size distributions of the metal nanoparticles, with a slight tailing toward larger sizes. A typical example is reported in Fig. 1.

From an overview of the TEM data reported in Table 2, two main trends are clear. First of all, considering the microgel with 15% clay (Table 2, entries 1–3), the average size of the Pd nanoparticles depends strongly on the nature of the reducing agent and increases on moving from NaBH₄ (3.8 nm) to ethanol (7.4 nm) and then to dihydrogen (12.8 nm). This effect is of course related to the reduction rate: the faster the metal ions are reduced, the more nuclei are produced which then grow to the final nanoparticles: since the amount of metal is the same in all cases, more nuclei at the reaction beginning means a higher number of smaller metal nanoparticles at the end. Thus, considering that the reduction rate decreases in the order NaBH₄ > ethanol > dihydrogen, the differences are well explained. Such observations allow also to infer that the microgel morphology has in this case a comparatively little influence on the final size of the metal nanoparticles. Indeed, in the case of other microgel systems, metal nanoclusters with almost the same sizes were produced irrespective of the employed reducing agent, which was explained in terms of steric constraints to nanoparticle growth imposed by the microgel network [5b,6].

Furthermore, it has to be remarked that in the case of NaBH₄ as the reducing agent the metal nanoparticles, although small and monodisperse, exhibit extensive aggregation in the TEM micrographs, whereas with ethanol as the reducing agents they invariably appear well isolated (Fig. 2).

The second consideration regards the effect of the different clay content on the nanocluster size: at 1% Pd content, a lower content of clay corresponds to a lower average size for samples reduced in ethanol (i.e. 7.4 nm, 4.5 nm, 3.1 nm average size for microgels with 15%, 10% and 5% clay, respectively; entries 2, 6 and 8, Table 2), whereas no differences were apparent for samples reduced with NaBH₄ (i.e. always 3.8 nm average size for microgel with 15% and 10% clay, respectively; entries 1 and 5, Table 2). Similarly, no differences with varying clay content were observed in samples reduced with ethanol at 5% palladium content (i.e. 7.5 nm, 7.6 nm, 7.6 nm average size for microgels with 15%, 10% and 5% clay, respectively; entries 4, 7 and 9, Table 2). Microgels with increased clay content are featured by a lower swelling degree, hence by a higher density of polymer chains in the microgel particles due to the presence of chemical and physical crosslinks between clay and microgel chains [7c]. Although steric constraints appear not to be a factor influencing nanoparticle growth within these microgels (see above), the different swelling degree can well affect the final nanoparticle size by determining the rate of the reduction/nucleation processes with the same reducing agent. Clearly, these processes are facilitated in microgels with a higher swelling degree, which are more accessible and pose less limitations to the diffusion of species through them; consequently, more nuclei, hence smaller nanoparticles, are formed in the microgels with the lowest content of clay, and this effect is particularly noticeable if the reducing agent is not very fast (ethanol vs. NaBH₄) and if the metal content is low (1% Pd vs. 5% Pd).

Of course, the nature of metal also plays a role in determining the final nanoparticles size, and in the absence of steric effects by the microgel network the rates of the reduction and nucleation processes become the decisive factor. Thus, use of Au or Pt precursors instead of Pd under otherwise identical conditions (nature of the microgel support, amount of metal precursor, solvent, reducing agent etc.) results in the case of Pt in metal nanoparticles with a marginally larger size compared to Pd, whereas much bigger nanoparticles are produced in the case of Au (entries 8, 11 and 12, Table 2).

The nanocomposite microgels with 5% and 15% clay content were characterized also from the point of view of their hydrodynamic

Table 1
Microgel/clay/metal nanocomposites prepared in this work.

Sample	Metal content (% w/w)	Clay content (% w/w)	Reducing agent
Pd1C15Na	1	15	NaBH₄
Pd1C15Et	1	15	EtOH
Pd1C15H	1	15	H₂
Pd5C15Et	5	15	EtOH
Pd1C10Na	1	10	NaBH₄
Pd1C10Et	1	10	EtOH
Pd5C10Et	5	10	EtOH
Pd1C5Et	1	5	EtOH
Pd5C5Et	5	5	EtOH
Pd10C5Et	10	5	EtOH
Pt1C5Na	1	5	NaBH₄
Au1C5Na	1	5	NaBH₄