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Core phosphine-functionalized amphiphilic nanogels as catalytic nanoreactors for aqueous biphasic hydroformylation

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ABSTRACT

Amphiphilic phosphine-functionalized nanogel particles were synthesized by aqueous polymerization-induced self-assembly insuring a well-defined architecture as well as a narrow size distribution (average diameter of ca. 90 nm in water). They were successfully applied as ligands for the biphasic hydroformylation of 1-octene catalyzed by rhodium, yielding TOFs in the 350–650 h^{-1} range and a linear to branched aldehyde ratio of 3.5. Embedding the phosphine ligands within a cross-linked structure did not strongly impede mass transfer toward the active centers, as proved by fast metal coordination and a catalytic activity tantamount to that of higher chain mobility micelles or core-cross-linked micelles that have phosphine moieties located on flexible linear arms. However, this extended cross-linking reduced particle swelling and transfer to the organic phase, affording a significantly lowered Rh loss. For all the architectures, a low functionalization degree was preferable to achieve high activity, the selectivity remaining essentially unchanged.

1. Introduction

Olefin hydroformylation is the World's largest industrial process making use of homogeneous catalysis, with an annual production volume in excess of 12 Mton [1–4]. This topic continues to stimulate intense research because of interest in developing an efficient transformation of the heavier α-olefins. Rhodium catalysts afford a much higher selectivity in favor of the greater added value linear product than the more commonly used cobalt carbonyl catalyst, but costs incurred in the recovery and recycling of the expensive metal make this process prohibitive. Rh-catalyzed hydroformylation is implemented on a large scale only for the lighter olefins (propene, butene) leading to sufficiently volatile aldehyde product amenable to cost-effective distillation [5,6].

An alternative approach is available through the aqueous biphasic Rhône-Poulenc/Ruhrchemie process where the rhodium catalyst is confined in the aqueous phase by binding to water-soluble triphenylphosphine trisulfonate (TPPTS) [7]. This approach allows inexpensive and efficient catalyst recovery by simple room temperature decantation. However, the reaction occurs at sufficient rate only for the lighter alkenes (once again, propene and butene) that have sufficient solubility in water where the reaction takes place [8]. For higher olefins with insufficient water solubility, mass transport severely limits the reaction rate, which can only slowly take place at the water/organic interface. Many stratagems have been explored to increase mass transport, homogenize the system

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Abbreviations: ACPA, 4,4′-azobis(4-cyanopentanoic acid); CCM, core-cross-linked micelle; CTPPA, 4-cyano-4-thiothiopropylsulfanyl pentanoic acid; DEGDMA, di(ethylene glycol) dimethacrylate; DPPS, 4-diphenylphosphinostyrene; M, micelle; MAA, methacrylic acid; NG, nanogel; PEOMA, poly(ethylene oxide) methyl ether methacrylate; S, styrene; TPP, triphenylphosphine.

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or increase the interface area, such as the addition of organic co-solvents [9,10], cyclodextrins [11–14], polymer lattices [15,16] or other surfactants [16–18], the use of thermomorphic solvent systems [19–21] or anchoring the metal catalyst to the hydrophobic part of surfactants that self-organize in micellar form [22–26].

We have recently introduced a new tool for application to the aqueous biphasic hydroformylation of higher olefins, consisting of the unimolecular equivalent of a self-assembled micelle [27–29]. This architecture was synthesized through a convergent approach using reversible addition-fragmentation chain transfer (RAFT)-mediated emulsion polymerization [30] in a three-step “one pot” preparation [27]. For convenience, the molecular structure of the polymer is shown in Fig. 1. Such technique made use of the polymerization-induced self-assembly (PISA) phenomenon to produce diblock copolymer micelles of controlled size the core cross-linking of which could be quantitatively achieved in a final step. The advantage of these objects with respect to the corresponding micelles is to remove the excessive nanoreactor swelling and the micelle-free surfactant equilibrium, which are known to negatively affect the catalyst recovery process and the catalyst leaching. More specifically, the new tool is a core-shell polymeric nanoreactor where the amphiphilic diblock copolymer arms are all tied together by cross-linking at the hydrophobic chain ends. We have named this new type of polymer architecture a “core-cross-linked micelle” or **CCM**. The hydrophobic blocks are functionalized with triphenylphosphine (TPP) ligands via incorporation of 4-diphenylphosphinostyrene (DPPS) as a comonomer to insure the catalyst binding and confinement within the polymer core, whereas the hydrophilic shell insures the nanoreactor confinement in the aqueous phase. The first application of these nanoreactors, symbolized as **TPP@CCM**, to the aqueous biphasic hydroformylation of 1-octene has demonstrated high activity [27]. A follow-up study has highlighted the efficient recycling and the weak contribution of mass transport kinetics to the reaction rate [29]. However, ICP-MS analysis of the recovered organic phase showed a metal leaching of ca. 2 ppm. Most intriguing, dynamic light scattering studies suggested that this leaching is related to transfer of the entire polymer scaffold to the organic product phase as larger agglomerates (coupled particles).

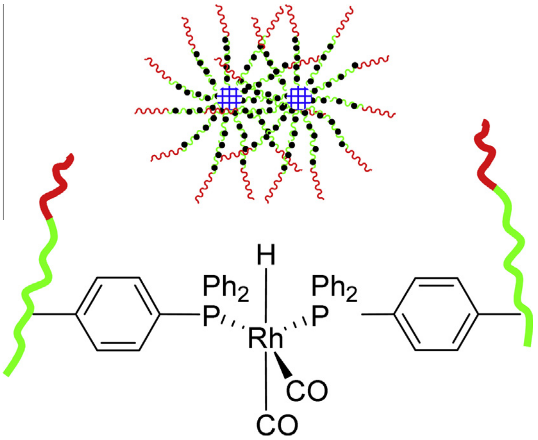

Fig. 2. Particle-particle coupling resulting from interpenetration and Rh-TPP coordination.

The particle-particle coupling process was proposed to occur via interpenetration leading to core-core contact, allowing the cores to be cross-linked by the metal complex, see Fig. 2. This is possible because the standard hydroformylation conditions impose the presence of a large fraction of free TPP sites (P/Rh = 4 was used in most catalytic tests) [27–29]. Of interest for an understanding of the leaching mechanism, the combined DLS and ICP-MS studies indicated a direct correlation between the amount of lost metal and the extent of particle-particle coupling. We have therefore engineered a modified nanoreactor architecture, consisting of an entirely cross-linked phosphine-bearing hydrophobic core. This modification is expected to disfavor the reaction of a rhodium center with two phosphine ligands from different particles and should therefore lead to reduced interparticle coupling and metal leaching. The principle of stopping interpenetration by nanogel cross-linking was demonstrated by Hawker, Fréchet and coworkers who reported a successful one-pot tandem transformation with one acid-catalyzed and one base-catalyzed step, using a combination of acid- and base-functionalized nanogels [31]. In this contribution, we report the synthesis of a new nanogel (**NG**) nanoreactor and its application to 1-octene hydroformylation. As will be shown, the architecture modification indeed leads to a significant reduction of catalyst leaching.

2. Experimental section

2.1. General

All manipulations were performed under an inert atmosphere of dry argon by using Schlenk line techniques. Solvents were dried by standard procedures and distilled under argon prior to use. 4,4′-Azobis(4-cyanopentanoic acid) (ACPA, >98%, Fluka), methacrylic acid (MAA, 99.5%, Acros), poly(ethylene oxide) methyl ether methacrylate (PEOMA, $M_n = 950\ \text{g mol}^{-1}$, Aldrich), di(ethylene glycol) dimethacrylate (DEGDMA, 95%, Aldrich), 4-diphenylphosphinostyrene (DPPS, 97%, Aldrich), 1,3,5-trioxane (Aldrich, >99%), acetylacetonatodicarbonyl rhodium(I), ([Rh(acac)

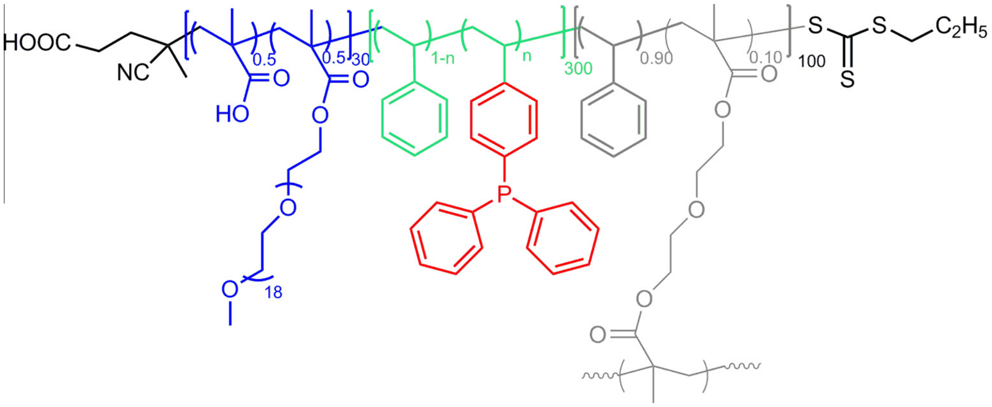

Fig. 1. Molecular structure of **TPP@CCM**.