



Aqueous phase homogeneous catalysis using core–shell nanoreactors: Application to rhodium-catalyzed hydroformylation of 1-octene



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ABSTRACT

High catalytic activity (turnover frequencies up to 700 h⁻¹) was achieved using new triphenylphosphine-functionalized core cross-linked micelles, TPP@CCM, as nanoreactors and [Rh(acac)(CO)₂] as catalyst precursor for the aqueous biphasic hydroformylation of 1-octene. While the hydrophobic core of the polymer offers an adequate environment for the catalytic reaction, its hydrophilic shell confines the catalyst into the aqueous phase and prevents extensive leaching toward the substrate/product phase. Selectivity is better than that of the homogeneous reaction catalyzed by the Rh/PPh₃ system, with minor isomerization and linear to branched aldehyde ratios (l/b) between 3 and 6. Various operating parameters, such as catalyst/ligand concentration, temperature, and P/Rh ratio, were varied and proved that these nanoreactors do not suffer from significant mass transfer limitations. The effect of the nanoreactor hydrophobic core size and degree of functionalization on activity and on l/b regioselectivity has also been investigated. The possible causes of catalyst leaching are discussed.

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1. Introduction

Biphasic catalysis is an elegant strategy of catalyst immobilization in which the catalyst is confined into a solvent slightly miscible or immiscible with the products, allowing fast separation of the catalytic phase by settling and easy recycling. Although there has been increasing research on the application of biphasic reaction media with innovative solvents—such as fluorinated solvents [1] and ionic liquids [2,3]—yielding successful developments like the Difasol process [4], use of water to solubilize the catalyst has the advantage of driving the system toward sustainability and diminishing costs. A well-established industrial application of the aqueous biphasic catalysis is the Ruhrchemie/Rhône Poulenc oxo process, in which propene is converted to butanal by a hydrosoluble rhodium complex. However, the same process cannot be applied to longer chain olefins (>C₄), their poor solubility in water

leading to poor reaction rates. Many strategies have been developed to overcome this issue, among which use of cosolvents [5–7] or phase transfer agents such as cyclodextrins [8,9] or activated carbons [10]. On the other hand, surfactants or amphiphilic ligands can also create organic substrate-rich nano-objects (micelles) within the aqueous catalyst phase. The latter yield more stable and more adequately tunable catalytic systems, but still the dynamic structure of the micelles results in catalyst loss at the interface and may also generate stable emulsions by excessive swelling of the micellar core [11,12]. In a novel approach recently introduced by us [13], both limitations have been removed by turning the self-organized and dynamic micellar architecture into a unimolecular polymeric core–shell nano-object by cross-linking the hydrophobic segments of self-assembled amphiphilic block copolymers. Hence, swelling of these particles is limited by the dimensions of the resulting macromolecule and the micellar equilibrium with the free arms is removed.

A few examples of unimolecular macrostructures that achieve a favorable environment for efficient catalysis in water are available in the open literature, yet with various architectures

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and levels of complexity. Using natural polyphenols as amphiphilic ligands, Mao et al. [14] could prepare noble metal complex and noble metal nanoparticle catalysts for the biphasic hydrogenation of cinnamaldehyde and quinoline. The authors observed some decrease of conversion upon recycling, whose extent depended on the content of polyphenols: from 61% to 97% of the original activity was retained after five runs. Gong et al. [15] synthesized four water-soluble dendritic phosphonated ligands starting from poly(amido amine) (PAMAM) dendrimers. The first ligand resulted from a partial functionalization of the dendritic surface with monophosphine moieties, the remaining amine functions enabling its dissolution into the aqueous phase. They also alternated phosphine and sulfonate functions to further increase phosphine loading while keeping enough water solubility. Finally, they grafted some long aliphatic chains to better interact with the olefin and enhance its solubilization into the aqueous phase. These various objects thus comprised a limited amount of phosphorus atoms (18 maximum per object), mainly located at the periphery. Their application to the hydroformylation of 1-octene led to relatively low turnover frequency (TOF) values ($<25 \text{ h}^{-1}$) and significant loss of rhodium, as indicated by the yellow coloring of the organic phase. Terashima et al. [16] proposed a different approach to incorporate monophosphine units into a star polymer, using controlled radical polymerization mediated by ruthenium. As the result of the simultaneous introduction of phosphine monomer, amphiphilic macroinitiator, and cross-linking agent, the phosphine ligands were here confined within the obtained polymer microgel core, entrapping ruthenium. These objects were successfully tested for Ru-catalyzed hydrogenation under a thermomorphic approach [17]. In a close strategy of catalyst confinement, Weck et al. [18] prepared shell cross-linked micelles containing catalytic Co(III) salen functions in the hydrophobic cores from amphiphilic triblock polymers. Applied to the hydrolytic kinetic resolution of epoxides, these catalysts exhibited substrate selectivity based on hydrophobicity, unlike their non-cross-linked analogs. They could also be successfully recycled eight times by ultrafiltration. L-Proline functionalized poly(methyl methacrylate) (PMMA) nanogel particles were also proposed by O'Reilly et al. [19] as catalysts for aldol reactions in water. An increase in the weight percentage of L-proline methacrylate incorporated in the nanogel particles from 2% to 10% strongly reduced their activity, while changes in the cross-linking density (CLD) in the 0.5–5 wt% range had only a minor effect. CLD as high as 50 wt% was indeed required to shut down the reaction. Moreover, the more hydrophobic the nanogel core, the higher the observed enantioselectivity. These examples prove that the performance and stability of such macrostructures require suitable loading and location of the catalytic moieties, as well as a good match between the hydrophobic character of the substrate and the polymer core.

In this study, triphenylphosphine (TPP)-functionalized core cross-linked micelles (TPP@CCM) were synthesized by a one-pot emulsion polymerization mediated by the reversible addition–fragmentation chain transfer (RAFT) technique, wherein the metal complex is located on the hydrophobic part of the polymer flexible arms. The method also allows great flexibility regarding the density of phosphine functions, their distribution within the object, the size of the core, and that of the hydrophilic layer. Our earlier contribution [13] has detailed the synthesis and characterization of these core-shell polymers and has provided indication of rapid mass transport of organic compounds across the hydrophilic barrier and into the hydrophobic core. It also proved them to be convenient ligands for the biphasic rhodium-catalyzed hydroformylation of 1-octene. The present paper gives a fuller and more detailed account of the catalytic results obtained varying different reaction parameters, such as catalyst/ligand concentration, temperature, P/Rh ratio,

as well as the density of phosphine within the objects and the molar mass of the hydrophobic segment, and discusses the driving mechanisms.

2. Materials and methods

2.1. Materials

[Rh(acac)(CO)₂] (99%, Alfa Aesar), 1-octene (99+%, Acros), *n*-nonanal (>97%, Alfa Aesar), *n*-decanal (>96%, Alfa Aesar), and anisole (99.0%, Fluka) were used as received. Carbon monoxide and dihydrogen were obtained from Linde Gas. Syngas was prepared by introducing equimolar amounts of CO and H₂ into a monitored gas reservoir feeding the autoclave reactor at constant pressure. The reference core cross-linked micelle used for the parametric reaction study was prepared as described in our previous contribution [13] and stored under an inert atmosphere.

Fig. 1 exhibits the detailed structure of the TPP@CCM made by convergent synthesis in water. The thin hydrophilic shell (degree of polymerization (DP) = 30) was formed by RAFT copolymerization of methacrylic acid and poly(ethylene oxide) methyl ether methacrylate. The subsequent hydrophobic part consisted of a styrene (S)/4-diphenylphosphinostyrene (DPPS) copolymer, with 300 units and a DPPS:S ratio of 1:9. The resulting amphiphilic block copolymers self-assembled into ca. 70 nm micelles in water. Addition of (di(ethylene glycol) dimethacrylate) (DEGDMA) cross-linker, together with additional styrene in a DEGDMA/S ratio of 1:9, allowed generating the TPP@CCMs as a concentrated latex suspension (27.3% solid content), containing 0.128 mol L⁻¹ of P. Slightly modified versions of the TPP@CCMs have now been synthesized by the same procedure with either longer hydrophobic chains (DP = 500) and the same DPPS:S ratio (1:9) or with the same DP for the hydrophobic chain (300) but different DPPS:S ratios (1:19 and 1:3). See the Supporting Information for the synthesis and characterization details.

2.2. Experimental procedure

2.2.1. Biphasic hydroformylation

A Hastelloy C276 autoclave equipped with a gas-inducing stirrer was used for the hydroformylation experiments. The volumetric ratio of organic to aqueous (including the TPP@CCM latex) phases was set to 3:1 (prior to swelling) for a total volume of 0.1 L. The organic phase consisted of a mixture of 1-octene (1.1 kmol m_{org}⁻³) and *n*-decanal to mimic the conditions within a continuous stirred tank reactor, where the out-flowing organic phase stream should be mainly constituted of C9 aldehydes, while allowing precise quantification of these products.

2.2.1.1. Standard reaction tests. First, Milli-Q water was introduced into a Schlenk tube and deoxygenated by nitrogen bubbling. The required quantity of TPP@CCM latex (according to desired P content) was added through a nitrogen-purged syringe, followed by stirring for 15 min. In order to swell the hydrophobic core of the nano-objects, 3 mL of *n*-decanal was added and the resulting mixture was stirred for an additional 15 min. Then, a separate solution containing [Rh(acac)(CO)₂] dissolved in 3 mL of *n*-decanal was added through a Teflon cannula, and the resulting mixture was stirred for 5 min. This colloidal suspension was then transferred into the autoclave, followed by the addition of the remaining *n*-decanal (56 mL) and 1-octene (81.6 mmol). The reactor was purged three times with 15 bar of nitrogen, checked for leak under N₂ pressure, and then purged four times with 15 bar of syngas (about 25 min for the whole procedure). It was subsequently heated under low syngas pressure (2 bar) and slow stirring speed

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