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Pickering Emulsions Based on Supramolecular Hydrogels: Application to Higher Olefins' Hydroformylation

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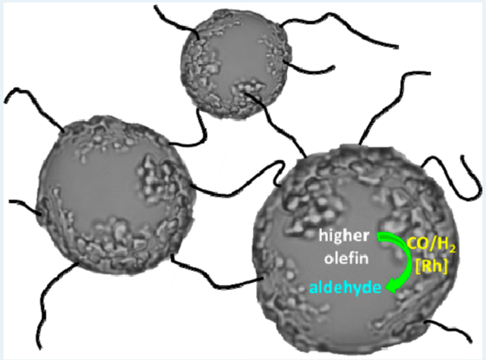
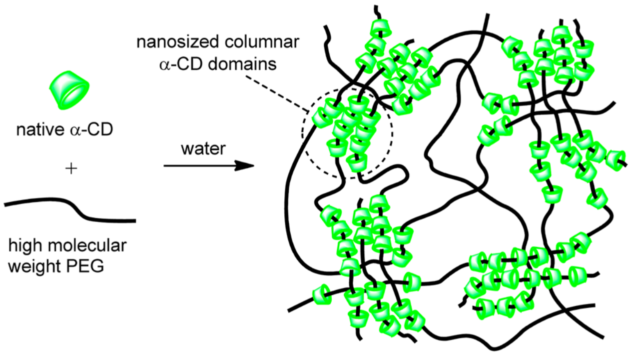
Supporting Information

ABSTRACT: Supramolecular hydrogels elaborated from a mixture of native α-cyclodextrin and poly(ethylene glycol)s in water proved to be effective media for higher olefins Rh-catalyzed hydroformylation due to the formation of Pickering emulsions.



KEYWORDS: *hydrogel, cyclodextrins, Pickering emulsion, biphasic catalysis, hydroformylation*

Scheme 1. Formation of a Supramolecular Hydrogel from α-CD and High-Molecular-Weight PEG[a]



[a]PEG thread into the α-CD cavity resulting in necklace-like polypseudorotaxanes.

After having been successfully used in biology and medicine,[1−6] supramolecular hydrogels currently find applications in other areas, such as materials[7−10] or catalysis.[11] In particular, supramolecular hydrogels have emerged as a promising class of hydrophilic media for catalysis because of the ease with which they could be implemented.[12−14] They were readily accessible by physical bindings between two complementary compounds through noncovalent interactions. In catalysis, the resulting three-dimensional cross-linked macromolecular networks have especially been used in the gel phase as solid-like structures to confine reactants in an organized environment and make them react selectively.[15−20] Astonishingly, catalytic applications in the sol phase have not been exploited so far. Recently, we have been very interested in several publications by Li et al.[12,21,22] They showed that supramolecular hydrogels built up from poly(ethylene glycol) (PEGs) and α-cyclodextrin (α-CD) contained nanosized columnar α-CD domains (nanocrystallites) acting as physical cross-links alongside PEG chains not included within the α-CD cavity (Scheme 1). Concurrently, Saito et al. showed that CD-based precipitates could help to form Pickering emulsions, that is, particle-stabilized emulsion.[23] The latter have recently gained renewed interest because they were considered an efficient alternative to solve mass transfer limitations in biphasic system.[24] Contrary to amphiphilic surfactants that form stable emulsions and require special equipment for separation,[25,26] Pickering emulsions act as emulsifiers and can be advantageously recovered by filtration once the reaction is complete. Taking into account the previous observations, we wondered how relevant the presence of crystallites in the sol phase of a α-CD/PEG hydrogel could be to form Pickering emulsions through contacts with an organic phase. Herein, we highlighted

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for the first time the ability of α-CD/PEG crystallites to form Pickering emulsions in the presence of an oil phase. The obtained Pickering emulsions found application in organometallic catalysis. They proved especially effective in the highly challenging aqueous Rh-catalyzed hydroformylation of higher olefins.

Hydrogels are prepared from aqueous saturated solutions of native α-CD and various amounts of PEGs with molecular weight of 20 000 g/mol (PEG20000) and 35 000 g/mol (PEG35000). The α-CD concentration is kept constant, and the PEG concentration is varied to yield a series of hydrogels with different stoichiometries. Their stability is evaluated by successive heat and cool cycles. Whatever the nature of the PEG (PEG20000 or PEG35000), α-CD/PEG hydrogels with a 2:1 stoichiometry prove to be inappropriate because a precipitation of the polypseudorotaxanes occurs. Conversely, sol−gel transitions always takes place for α-CD/PEG hydrogels with a 1:1 stoichiometry, even after 10 successive heat and cool cycles. For both α-CD/PEG20000 (**H1**) and α-CD/PEG35000 (**H2**) hydrogels in a 1:1 stoichiometry, a sol−gel transition temperature of ca. 38 °C is measured. The existence of crystallites is confirmed over a wide temperature range from room temperature to 85 °C. First, the observed turbid sol is indicative of still existing packed α-CD/PEG polypseudorotaxane domains in the mixture, as already described in the literature.[27] Second, X-ray diffraction measurements clearly show the existence of crystallites in both the gel and the sol (ESI) because no significant change in the diffraction spectra can be noted below and over the sol−gel transition temperature. Third, optical microscopy reveals crystalline objects even at high temperature (ESI). Information is also collected on the supramolecular hydrogels' behavior in the presence of an oil phase. Optical microscopy realized on a 1-decene/**H1** mixture clearly shows three different phases (Figure 1a).

Almost no crystallites can be observed in the upper organic phase (Figure 1b). Conversely, crystallites and an oil in water (O/W) emulsion coexist in the middle phase (Pickering emulsion, Figure 1c). The hydrogel lower phase, for its part, reveals the exclusive presence of crystallites (Figure 1d). An aliquot of the O/W emulsion sampled at 80 °C and observed at 20 °C is especially illustrative of the crystallites' adsorption onto the droplet surface (Figure 1f). Indeed, when cooling the system to room temperature, the small droplets observed at 80 °C coalesce to give larger droplets (compare Figure 1c, e, and f). Concurrently, the crystallites' size also increases. Crystallites are located at the water/oil interface.

The α-CD/PEG hydrogels have been used as reaction media in the Rh-catalyzed hydroformylation of 1-decene (**1**), 1-dodecene (**2**), 1-tetradecene (**3**), 1-hexadecene (**4**), and 1-octadecene (**5**) (Figure 2). The reaction proceeds at 80 °C under 50 bar CO/H_2 with $Rh(CO)_2(acac)$ as a rhodium precursor. The multiphase gas−liquid-sol system consists of syngas, the substrate-containing organic phase, and the supramolecular hydrogel in the sol phase. Immobilization of Rh-species within the supramolecular hydrogel is achieved thanks to a water-soluble ligand; namely, the trisodium salt of the trisulfonated triphenylphosphane (TPPTS).

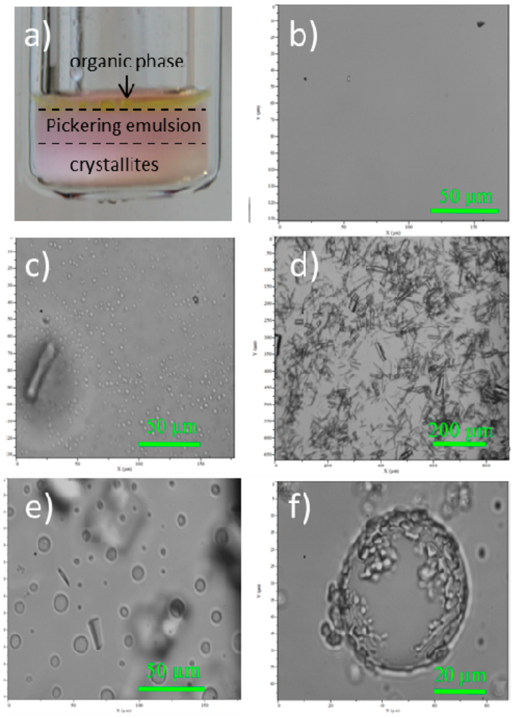

Figure 1. (a) Three-phase system at 80 °C of a 1-decene (0.6 mL)/**H1** (3 mL) mixture. The benchmark chromophore Red 1 has been added within the mixture to help visualization of the Pickering emulsion. (b−f) Optical microscopy of a 1-decene (0.6 mL)/**H1** (3 mL) mixture. (b) 1-Decene (upper yellow organic phase) at 80 °C. (c) Pickering emulsion (middle pink phase) at 80 °C. (d) **H1** sol phase at 80 °C (crystallites-containing phase). (e) Pickering emulsion sampled at 80 °C and observed at 40 °C. (f) Pickering emulsion sampled at 80 °C and observed at 20 °C.

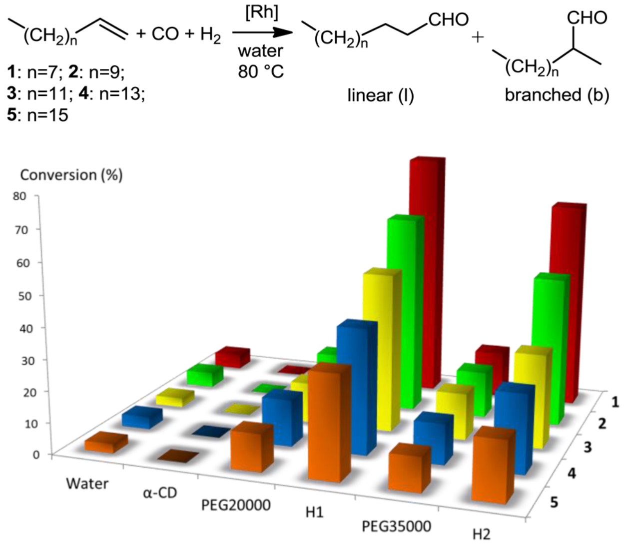

Figure 2. Rh-catalyzed hydroformylation of higher olefins **1**−**5**. Conditions: Rh/TPPTS/substrate = 1:5:140, 80 °C, 50 bar CO/H_2, 3 h reaction time.

Blank runs show very little conversion of 1-alkenes in the presence of α-CD because of the precipitation of α-CD/substrate complexes in the sol. Similarly, the use of PEGs as reaction media also leads to very low conversions. Conversely, because of the formation of a Pickering emulsion, the conversions obtained using α-CD/PEGs supramolecular hydrogels **H1** and **H2** are significantly improved when compared with those obtained without any additive (solely water) or with the separated components (α-CD or PEGs). For example, conversion of 1-decene is 16-fold that observed in neat water and 4-fold that measured using PEGs as additives. All the studied olefins take benefit from the α-CD/PEG crystallites-stabilized Pickering emulsion, irrespective of their alkyl chain length; however, a regular decrease in the conversion is observed when increasing the length of the substrate alkyl chain. Anyway, as clearly demonstrated by the increase in catalytic activity, the presence of α-CD/PEGs crystallites in the medium favors the existence of a particle-stabilized emulsion for which the surface contact at the aqueous/organic interface is significantly improved, resulting in accelerated reaction rates between the terminal olefins and the Rh catalyst.

A careful analysis of the reaction profiles in time shows that the conversions level off after 4 h reaction time, whatever the substrate (ESI). These results can be explained by previous studies on Pickering emulsions showing that particles can strongly adsorb at the aqueous/organic interface and inhibit the mass transfer between the two phases.[28−30] In the present case, α-CD/PEG crystallites play a role similar to particles and saturate the interface. A very different behavior would have been observed if α-CD/PEG mixtures had behaved as surfactants. Indeed, no mass transfer limitation is observed using surfactant-based emulsions.[31,32] However, this saturation phenomenon can be easily overcome by successive depressurization−pressurization sequences and heat and cool cycles. Indeed, after partial depressurization to 5 bar CO/H_2, the oil droplets coalesce upon cooling to 20 °C and creep into the upper organic phase (decantation). When subsequently heating the system at 80 °C under 50 bar CO/H_2, the conversion increases again for another 4 h period. The depressurization−pressurization sequences and heat and cool cycles can be repeated until most C═C double bonds are converted. Figure 3 is illustrative of this step-by-step conversion with 4 as a substrate.

For each cycle, 40−45% of remaining 4 can be sequentially converted, thus explaining the shape of the green curve. Moreover, the initial catalytic activity is recovered after each depressurization−pressurization cycle, thus demonstrating the integrity of the Rh catalyst during the course of the reaction.

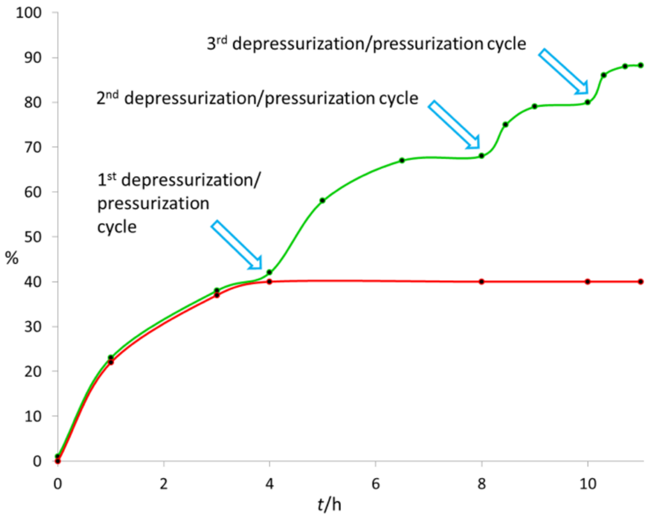

Figure 3. Conversion variation observed in Rh-catalyzed hydroformylation of 4 submitted to (i) one catalytic run (red curve) and (ii) successive depressurization−pressurization sequences and heat and cool cycles (green curve). Conditions: Rh/TPPTS/4 = 1:5:140, 80 °C, 50 bar CO/H_2.

Accordingly, the substrate conversion depends on only the interfacial saturation with time. Subjected to partial depressurization, the Pickering emulsion is broken, and dynamics of exchange at the aqueous/organic interface is then recovered.

In terms of chemoselectivity, the aldehyde proportion is always higher in the presence of hydrogel **H1** (ESI). Effects are especially marked for short alkyl chain olefins, such as 1-decene, for which the chemoselectivity rises from 59% without any additive (mainly alkene isomers are formed alongside the expected aldehydes) to 95% with **H1** as a reaction medium. The regioselectivity, for its part, remains rather constant, whatever the substrate (in the 2.3−2.9 range), suggesting that the hydrogel network does not significantly modify the equilibriums existing between the rhodium catalytic species (ESI).[33,34] The latter being unaffected, the aldehyde proportions are similar to those obtained without any hydrogel. This observation contrasts sharply with what is usually observed when β-CD derivatives and TPPTS are mixed together in water. A significant decrease in the l/b ratio is observed in that case because of the formation of a β-CD/TPPTS supramolecular complex.[33,34] In the present case, the utilization of α-CDs instead of β-CDs prevents the formation of such complexes and warrants the catalyst integrity.

Using **H2** as reaction media, conversions are adversely affected when compared with **H1** (Figure 2). Indeed, though the α-CD/PEG ratio between **H1** and **H2** remains constant, lengthening the PEG chains disfavors the crystallites' formation because they experience more difficulties in threading into the α-CDs cavity. No significant variations can be measured using **H2** in terms of chemo- and regioselectivities when compared with **H1**.

This preliminary investigation highlights the potential applications of supramolecular hydrogels, especially in the field of aqueous catalysis. The present study shows that O/W emulsions can be efficiently stabilized by α-CD/PEG crystallites. The resulting increase in contact surface between the substrate-containing organic phase and the catalyst-containing aqueous phase allows for a significant improvement in the catalytic performances. Thus, the existence of Pickering emulsions resulting from supramolecular hydrogel/oil phase mixtures is of prime importance and could play a pivotal role in improving the catalytic performance in many other systems. Further investigations are currently ongoing to extend the scope of the concept to other organometallic reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Preparation of hydrogels, viscosity measurements, optical micoscopy, X-ray diffraction measurements, and details of catalytic experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

H1, α-CD/PEG20000 hydrogel; **H2**, α-CD/PEG35000; TPPTS, sodium salt of the trisulfonated triphenylphosphane

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