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Letter

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Supramolecular Emulsifiers in Biphasic Catalysis: The Substrate Drives Its Own Transformation

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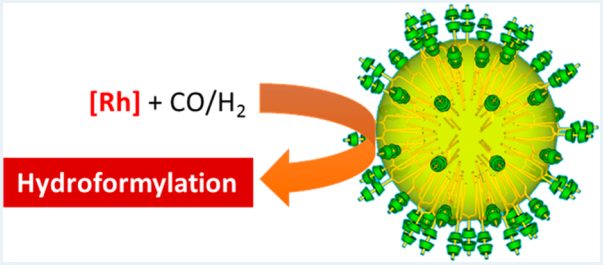
Supporting Information

ABSTRACT: Naturally occurring triglycerides have been hydroformylated through supramolecular means in the presence of cyclodextrins (CDs). During the course of the reaction, a transient supramolecular complex is formed between triglyceride alkyl chains and the appropriate CDs in a well-defined concentration range. The resulting CD/triglyceride supramolecular emulsifiers help convert the triglyceride C═C double bonds in biphasic conditions using a water-soluble organometallic catalyst. The catalytic system could be efficiently recycled.

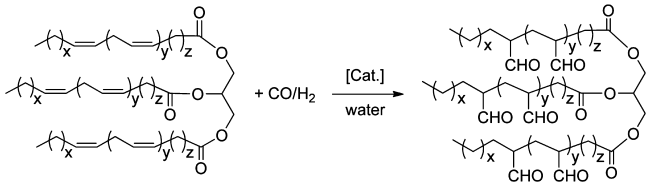


KEYWORDS: *aqueous-phase catalysis, triglycerides, cyclodextrin, emulsifier, hydroformylation*

Biomass has become an alternative source for production of chemicals. Of particular interest for industry is the conversion of naturally occurring triglycerides into high-value-added products that are not easily accessible from petroleum resources. Triglycerides are promising biosourced building blocks because they are renewable, eco-friendly, and produced easily in countries where their derived products can be directly used and valorized without the need for costly transportation. Moreover, contrary to petroleum derivatives that contain a limited number of atoms, triglycerides consist of long alkyl chains (>16 carbons). Accordingly, their conversion leads to functionalized products with a high proportion of carbon atoms that especially find application in the synthesis of plasticizers,[1] polymers,[2] and lubricants.[3] Hydroformylation[4] offers an effective way to access functionalized triglycerides (Scheme 1).

Indeed, hydroformylation of the triglyceride C═C double bonds leads to aldehydes that can be subsequently reduced or oxidized into alcohols, amines or carboxylic acids.[5] Few articles have been published so far on the hydroformylation of triglycerides, and most of them have dealt with the use of organic solvents. The first studies date to the 1960s and 1970s.[6]

Scheme 1. Aqueous Rh-Catalyzed Hydroformylation Reaction of Triglycerides[a]



[a]The location of the formyl group was chosen arbitrarily for clarity. The formyl group could also be located ont the left adjacent carbons.

More recent investigations have revealed the potential of hydroformylation of triglycerides in mild conditions.[7] Conversely, only one article has reported triglyceride hydroformylation in aqueous biphasic media.[8] Intuitively, it seems, indeed, impossible to convert a triglyceride using water as a solvent because of obvious solubility problems; however, given our expertise in the field of cyclodextrins (CD) and aqueous catalysis,[9] we anticipated that a self-emulsifier resulting from the supramolecular interaction between CDs and triglycerides could be advantageously used to develop a self-driven catalytic process in water.

Herein, we show that the formation of a CD/triglyceride supramolecular complex by inclusion of one of the triglyceride alkenyl chains into the hydrophobic CD cavity during the course of the reaction helps overcome mass transfer problems (Figure 1). Upon stirring, the CD/triglyceride supramolecular complex acts as a self-emulsifier that significantly increases the surface area between the triglyceride organic phase and the catalyst-containing aqueous phase. Because hydroformylated triglycerides do not interact with CDs, the product and the catalyst can be recovered separately by simple decantation once the reaction is complete. The proof-of-concept was implemented using triolein (T) as a triglyceride model substrate.

The key point of this supramolecular approach lies in a judicious choice of CDs. The supramolecular interaction of native (nonmodified) CDs with triglyceride alkyl chains has already been described,[10] but the obtained supramolecular amphiphiles were far too stable and precipitated, thus limiting their use as self-emulsifiers in aqueous catalysis. In this context, our idea was to use modified β-CDs that are well-known to

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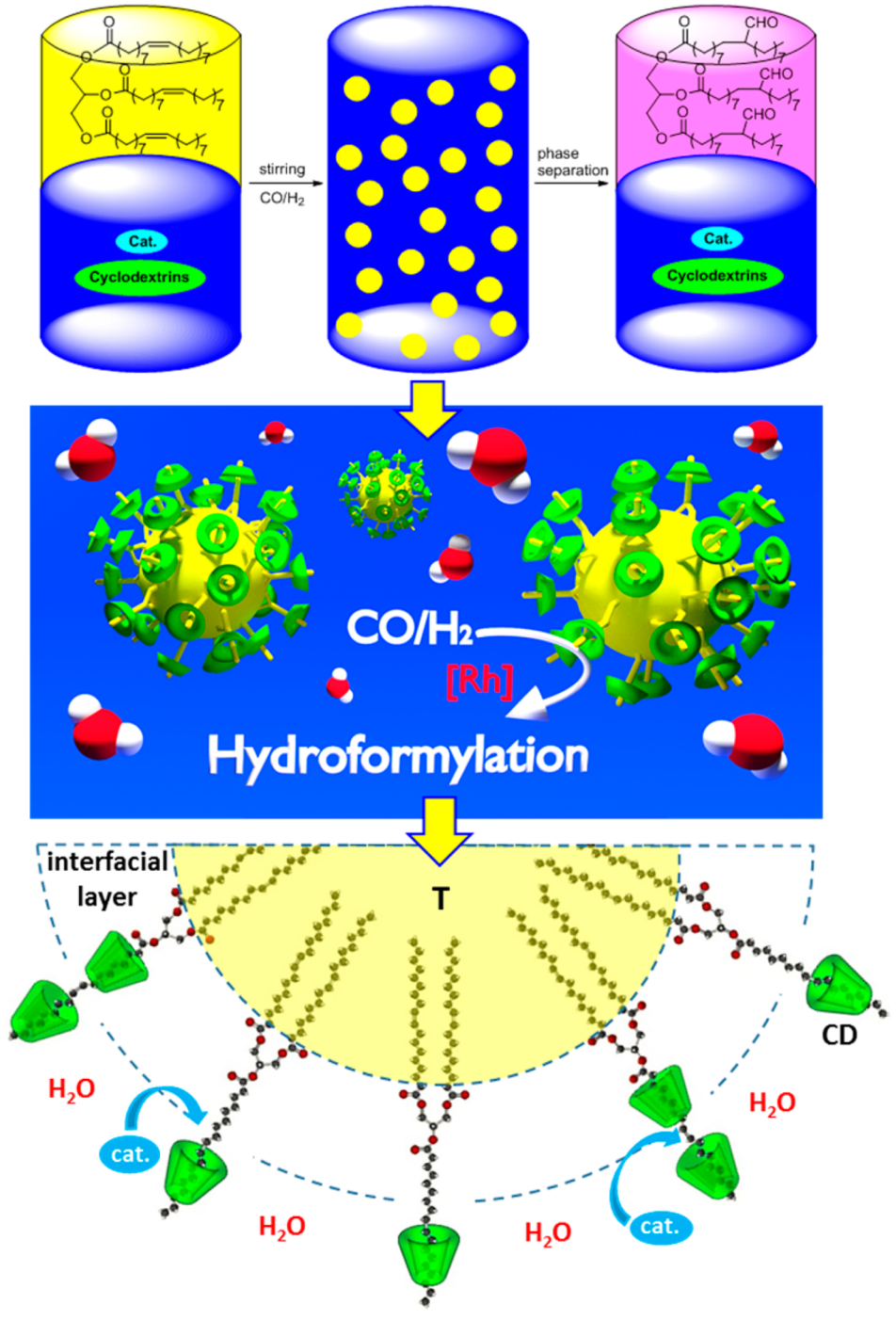

Figure 1. CD-assisted metal-catalyzed functionalization of triolein (T) in aqueous medium. CDs are cyclic oligomers consisting of six (α), seven (β), and eight (γ) glucose units bridged through 1,4-glycosidic bonds. They have a cone-shaped chemical structure with a hydrophobic inner cavity that allows CDs to incorporate other molecules. CDs are represented in green. cat. = water-soluble organometallic catalyst.

weakly interact with linear organic substrates.[11] Our choice fell on three partially substituted CDs: namely, the randomly methylated (RAME) β-CD, the hydroxypropylated (HP) β-CD, and a methylated β-CD substituted on the C2 hydroxyl group (CRYSMEB) (Table 1).

Considering triolein as a model substrate, our first goal was to verify the surface active character of the three modified CD/T couples. Surface tension measurements were carried out at the T/water interface (Figure 2). RAME-β-CD, HP-β-CD, and CRYSMEB behave similarly. The asymptotic variation of the surface tension γ resulting from an increase in the CD concentration clearly indicated a saturation of the T/water interface. As already shown for interactions between native CDs

Table 1. Description of Modified β-CDs Used in the Present Study

CD	substituent (R)	carbons bearing R	av no. R per CD
RAME-β-CD	$-CH_3$	2, 3, 6	12.6
HP-β-CD	$-CH_2-CHOH-CH_3$	2, 3, 6	5.6
CRYSMEB	$-CH_3$	2	5.6

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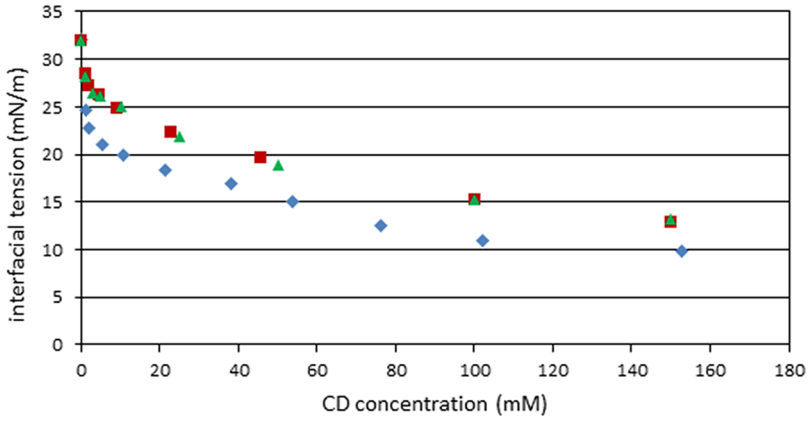

Figure 2. Variation of the interfacial tension (γ) at the T/aqueous interface with the concentration in RAME-β-CD (blue), HP-β-CD (red) and CRYSMEB (green) at RT.

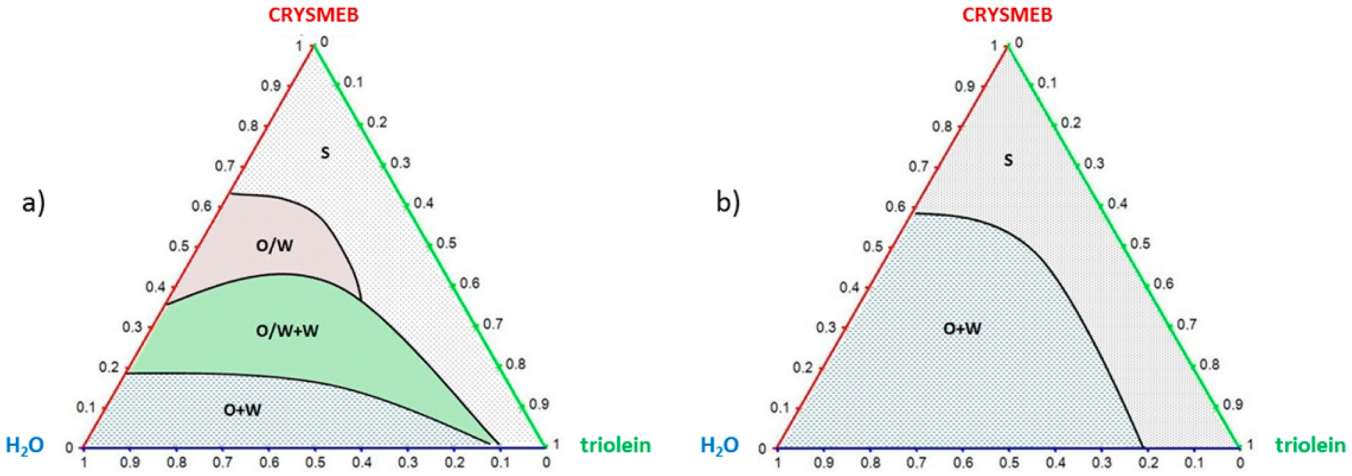

Figure 3. Phase diagrams of CRYSMEB as a function of the resting time: (a) 2 min and (b) 90 min.

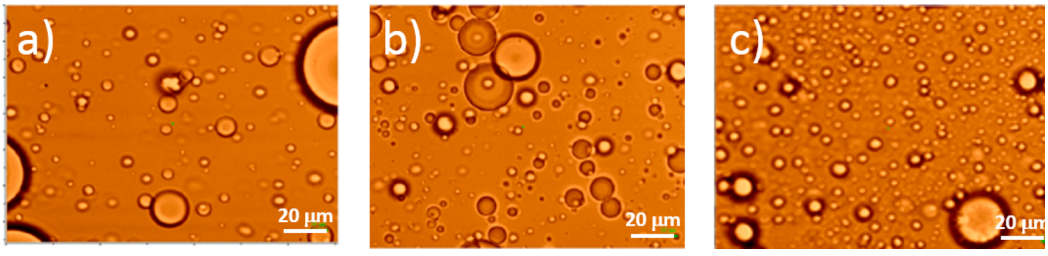

Figure 4. Optical microscopy performed at 22 °C of mixtures containing T (0.1 mL) and (a) RAME-β-CD (230 mg, 0.17 mmol), water (0.43 mL); (b) HP-β-CD 230 mg, 0.16 mmol), water (0.43 mL); (c) CRYSMEB (230 mg, 0.18 mmol), water (0.8 mL).

and triglycerides,[12] the saturation process resulted from the formation of surface-active T⊂CD$_n$ complexes for which the cis-monounsaturated alkenyl chains of T were included into at least one modified CDs. From the γ variations and the Gibbs equations, both the interfacial excess and interfacial area could be determined for each CD/T couple (Supporting Information). From these data, the CD/T stoichiometries could be calculated and were found to be 1/1, 1.5/1, and 2/1 for RAME-β-CD, HP-β-CD, and CRYSMEB, respectively.

The surface-active character of the CD/T supramolecular complexes was also confirmed by ternary phase diagrams constructed from CD/T/water mixtures at 80 °C (temperature at which the hydroformylation reaction proceeded). CD/T/water mixtures in various proportions were vigorously shaken for 5 min. When stirring was stopped, the ternary phase diagrams rapidly evolved with time. Figure 3 is illustrative of these time-dependent variations with CRYSMEB as additive. After 2 min resting time, varying the relative proportions of CRYSMEB, T, and water allowed determining four different areas on the graph (Figure 3a): O + W = a two-liquid phase; O/W + W = an unstable oil-in-water emulsion + a separated water phase; O/W = an unstable oil-in-water emulsion; and S = a solid-containing phase. Note that O/W and O/W + W evolved over time to give an O + W biphasic system (full decantation over 90 min, Figure 3b).

The CD/T/water mixtures were further characterized by optical microscopy (Figure 4). Although few large droplets were observed with RAME-β-CD (Figure 4a), HP-β-CD

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showed intermediate-sized bubbles (Figure 4b), and numerous small bubbles were observed for CRYSMEB (Figure 4c). Accordingly, the surface area between the aqueous and organic phases was rather low for RAME-β-CD, intermediate for HP-β-CD, and high for CRYSMEB.

Note that, concurrently to T, the surface activity of the fully hydroformylated product (**A**) was also assessed (Supporting Information, Figure S5). Only a very slight decrease in the surface tension, γ, could be detected supportive of the very weak affinity of **A** with the CD cavity. This probably resulted from the bulkiness of the formyl methyl groups that prevented inclusion of the functionalized alkyl chain into the CD cavity. Accordingly, as expected, the hydroformylated chains of **A** are not able to interact with the CD cavity.

The effects of the CD/T combination were assessed in the Rh-catalyzed hydroformylation of the C═C double bonds of T. The Rh complex was stabilized in water by coordination with the benchmark sodium salt of the trisulfonated triphenylphosphane (TPPTS). The CD/T/catalyst mixture was stirred in an autoclave at 80 °C under 80 bar CO/H_2. The relative proportions of CD, T, and water were varied to guarantee the CD water solubility (CD amounts <50% wght) and the existence of an O/W emulsion upon stirring. The catalytic results clearly demonstrated the viability of the concept of self-assembled supramolecular emulsifier because a significant increase in the conversion was observed whatever the CD when the CD molar concentration raised (Figure 5).

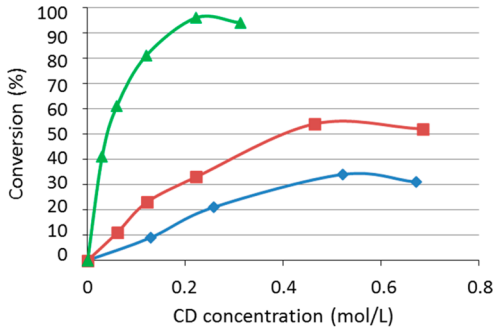

Figure 5. Conversion variation of the Rh-catalyzed hydroformylation of T as a function of the CD molar concentration for RAME-β-CD (blue), HP-β-CD (red) and CRYSMEB (green). Conditions: T (1 mL, 1 mmol), $Rh(CO)_2(acac)$ (3.9 mg, 0.015 mmol), TPPTS (42 mg, 0.075 mmol), water (3.4 mL for RAME-β-CD (blue) and HP-β-CD (red), 8.2 mL for CRYSMEB (green)), 6 h, 80 °C, 80 bar CO/H_2.

The rapid formation of the T⊂CD complex led to a transient O/W emulsion in which the T/water interface was greatly extended, thus favoring contacts between the triolein C═C double bond and the Rh catalyst. Note that there was no need to unnecessarily add too many CDs in the medium because the conversion slightly decreased for high CD concentrations, a result in line with the interfacial saturation phenomenon revealed by tensiometry (Figure 2).

More information about how the system proceeded was given from kinetic considerations (Supporting Information). A first-order variation of the conversion with the CD initial concentration was observed, suggesting that the hydroformylation occurred via a 1/1 CD/T supramolecular complex under a dynamic regime (catalytic conditions). In fact, because of the high catalytic activity of the Rh-catalyst, the lifetime of the T⊂CD complex was likely short, preventing the formation of a $T⊂CD_2$ complex. The rate at which the T⊂CD complexes were formed at the aqueous/organic interface thus explained the catalytic results depicted in Figure 5. The better result obtained with CRYSMEB probably resulted from its low substitution degree (Table 1). Indeed, association and dissociation processes between CRYSMEB and nonfunctionalized or functionalized T chains were greatly favored compared with the more bulky structures of HP-β-CD and RAME-β-CD, for which the inclusion processes were hampered by the CD substituents.

Not only did the formation of T⊂CD complexes impact the conversion, but it also positively affected the aldehyde selectivity (up to 97%, Supporting Information, Figure S8 and Table S1). Although the increase in conversion was clearly expected, the increase in the aldehyde selectivity constituted an unexpected result and reflected the local confinement of the partners (reactants, catalyst, CD) in the interfacial layer during the catalytic process. More precisely, the steric congestion resulting from the presence of the bulky CDs at the aqueous/organic interface forced the rhodium catalyst to proceed through a unique reaction pathway.[13] The aldehyde proportions were thus greatly enhanced. Moreover, the higher aldehyde selectivity observed with CRYSMEB resulted from the lifetime of the CRYSMEB/T supramolecular complex at the interface. The faster association and dissociation processes occurring in the CRYSMEB/T complex gave just enough time to the Rh catalyst to hydroformylate the C═C double bond before the aldehyde was released in the organic phase. Thus, the lower the lifetime at the interface, the higher the aldehyde selectivity. Note that changing the stoichiometry of the CO/H_2 mixture to 1/2 or 2/1 did not affect the conversion (95% and 96%, respectively, Supporting Information, Table S1) but strongly impacted the aldehyde selectivity (86% and 74%, respectively). Indeed, excess H_2 favored the direct hydrogenation of the C═C double bonds, whereas excess CO displaced the equilibriums toward low-phosphane coordinated rhodium species, which were less selective of the hydroformylation reaction.[14]

In addition to the improvement in the catalytic performance, the use of modified CDs also allowed for an easy reusability of the catalyst. Actually, once the stirring was stopped, a rapid decantation occurred within a few minutes (as already commented through the phase diagrams). The decantation is all the more effective because the hydroformylated T chains have very little affinity with the CD cavity. The catalytic phase was recovered and reused three times without significant loss of either catalytic activity or aldehyde selectivity (Supporting Information, Table S1).

Once the proof-of-concept was complete with T as a model substrate, the self-emulsifying process was extended to other unsaturated oils, such as sesame, sunflower, or olive oils (Supporting Information, Tables S2 and S3). Here again, CRYSMEB proved to be the best additive, especially to convert olive oil (86% conv., 86% aldehyde sel. within 6 h).

In conclusion, we found that the C═C double bonds of triglycerides can be readily converted into aldehydes using an aqueous biphasic system for which an organometallic Rh complex is retained within the aqueous compartment. The triglycerides drive their own conversion because of the transient formation of surface active CD/triglyceride supramolecular complexes. CRYSMEB especially proved to be very effective in this context.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00861.

Additional experimental details including materials and methods, formation of CD/**T** supramolecular complexes, interfacial excess, interfacial area, stoichiometry, catalytic experiments, NMR spectra, and kinetics (PDF)

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Notes

The authors declare no competing financial interest.

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