DOI: 10.1002/cssc.201300081

Versatile Eco-friendly Pickering Emulsions Based on Substrate/Native Cyclodextrin Complexes: A Winning Approach for Solvent-Free Oxidations

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Solvent-less Pickering emulsions were developed and applied to catalytic oxidation. These systems are stabilized by inclusion complexes between cyclodextrins and substrates, forming a 3D network among the dispersed phase. In the presence of hydrogen peroxide as a green oxidant and $[Na]_3[PW_{12}O_{40}]$ as a catalyst, they provide particularly efficient reaction media for the oxidation of olefins, organosulfurs, and alcohols. The reactions proceed at competitive rates (up to 400 h^{-1}) with straightforward separation of the phases by centrifugation or heating. Moreover, these new eco-friendly systems work at a preparative scale (up to 2.5 M) and are recycled without loss of activity.

Introduction

During the last two decades, the green chemistry concept has emerged as a very important topic for sustainable chemistry.[1] It is framed by a set of principles, such as 1) the design of processes to minimize the amount of byproducts and wastes, 2) the use of safe and benign reactants and solvents, and 3) catalytic processes. Generally, it is very difficult to reconcile all these principles in a single process. For example, organic reactions often require organic solvents; thus the substitution of hazardous solvents for eco-friendly ones, or even removing the solvent completely, is a key point in the development of a green process. In addition, to avoid chemical waste, the replacement of stoichiometric processes by catalytic systems that exhibit both high selectivity and activity becomes more and more clear.[2] In this context, catalytic oxidation plays a central role in the fine-chemical industry.[3] Polyoxometalates (POMs) are efficient catalysts for the selective oxidation of substrates by hydrogen peroxide; a green reactant that generates only water as the byproduct.[4] A large variety of processes based on POMs and H_2O_2 have been explored in recent decades that involved mesoporous materials,[5] dendrimers,[6] hyperbranched polymers,[7] phase-transfer catalysts (PTCs),[8] and ionic liquids.[9] In aqueous biphasic media, the catalytic performance of POMs depends on the solubility of the peroxo-POM species in the organic phase. To enhance the mass transfer of the anionic POM catalyst between the two phases and to enhance the water/oil (W/O) interfacial area, cationic PTCs, such as hydrophobic onium, salts are added.[8] Despite the numerous advantages of phase-transfer catalysis, two serious drawbacks can be highlighted: 1) the recovery of the PTC and catalyst from the reaction mixture is often troublesome, and 2) the toxicity of the PTCs as cationic amphiphiles. Indeed, numerous studies mentioned that PTCs resulted in skin irritation, hemolysis, environmental pollution, and so forth.[10] One way to circumvent these drawbacks consists of immobilizing the catalyst on various supports.[5–7] However, this strategy requires several synthetic steps. On the other hand, in 1991, Shimada et al. reported that cyclodextrins (CDs) could be used as emulsifiers.[11] CDs are biodegradable and biocompatible cyclic oligomers of D-glucopyranose and are described as shallow truncated cones with a hydrophobic cavity that can be used to form inclusion complexes (ICs; Figure 1).[12] Recently, Saito et al. reported the formation of stable emulsions using CDs instead of the commonly and largely used surfactants.[13] The presence of various oil phases (e.g., *n*-alkane or *n*-alkanol) results in the formation of oil/CD insoluble ICs. These solids, which are partially wettable by both water and oil, adsorb onto the W/O interface between the two phases and allow the formation of Pickering emulsions.[13,14]

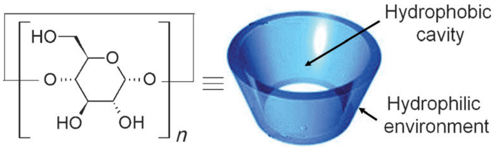

Figure 1. Structure of the native CDs [$n=6$ (α-CD), 7 (β-CD), or 8 (γ-CD)] and their schematic representation.

Despite their specific advantages, Pickering emulsions have rarely been applied to catalysis.[15] The few examples described in the literature report the use of Janus silica nanoparticles,[15a,b,c] amphiphilic POMs,[15d] carbonaceous microcapsu-

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Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201300081.

les,[15e] and polymersomes.[15f] Herein, we report the first catalytic Pickering emulsions based on CDs for the epoxidation of alkenes and the oxidation of sulfides and alcohols. The concept is based on a catalytic emulsion constituted of only the substrate, which plays the role of the oil phase, water, and the CD. In the present case, the catalyst is the water-soluble $[Na]_3[PW_{12}O_{40}]$ POM and the oxidizing agent is H_2O_2. The emulsion is stabilized by solid substrate/CD complexes. The solvent-free microstructured reaction medium is particularly relevant in terms of catalytic activity, workup, and recycling; this makes it a particularly attractive eco-friendly system for oxidation at the preparative scale.

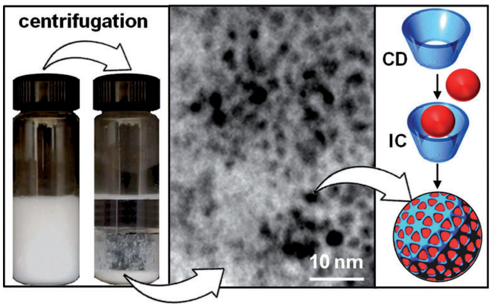


Figure 2. TEM imaging the structural morphology of the β-CD/**1** nanoparticles separated from the **1**/water/β-CD emulsion by centrifugation and their mechanism of formation.

Results and Discussion

In the presence of α-, β-, and γ-CDs, and after emulsification (11 500 rpm during 60 s with an Ultra-Turrax instrument), the cyclooctene (**1**)/water biphasic system provides whitish, stable emulsions for particular compositions. The electrical conductivity of the resulting emulsions indicates a water external phase, that is, O/W emulsions. Moreover, centrifugation (4000 rpm for 5 min) allows rapid and distinct separation of the three phases: water, **1**, and a white powder. After removal of the two liquids, analysis of the dried powder by ^{1}H NMR spectroscopy revealed that it was composed of an equimolar mixture of CD and **1**, suggesting the formation of 1:1 ICs. This is in good agreement with the results reported by Yujuan and Runhua ($K_{\beta\text{-CD/1}} = 706.5\ \text{M}^{-1}$).[16] TEM was used to image the structural morphology of the precipitated fraction (Figure 2). The structure reveals spherical nanoparticles (3.6 nm) formed from ICs (≈46±20 ICs/particles). Based on the results reported by Davarpanah and Vahabzade, we can assert that these solid particles act as an emulsifier in our system.[14]

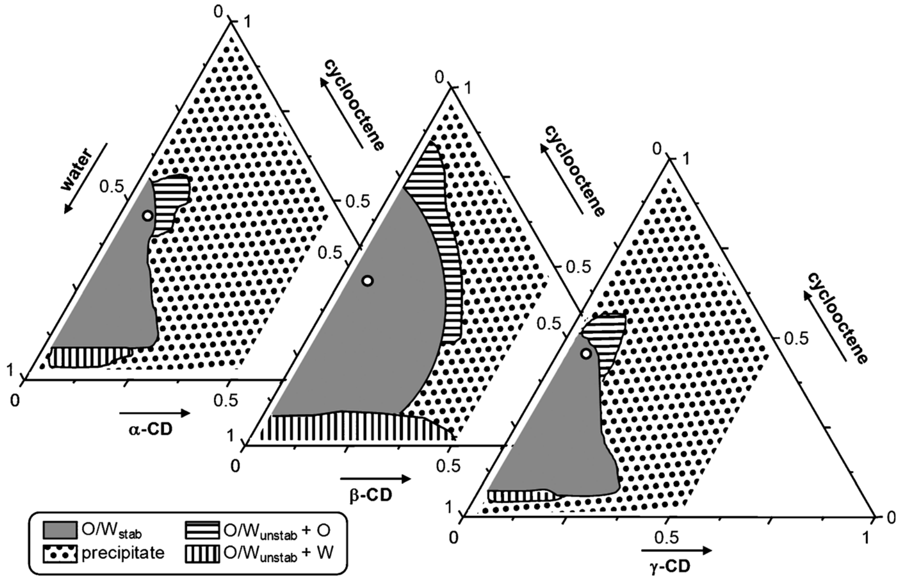


Figure 3. Ternary phase diagrams of the **1**/water emulsion stabilized by α-, β-, and γ-CD at 25 °C. The composition is represented in weight fractions. The white circles correspond to the composition used to perform the catalytic reactions.

The ternary phase diagrams of the **1**/water system stabilized by α-, β-, and γ-CDs are presented in Figure 3. Four different types of behavior are observed, depending on the ratio between the three components: 1) a stable O/W emulsion (O/W$_{stab}$), 2) an unstable O/W emulsion with a separated water phase (O/W$_{unstab}$+W), 3) an unstable O/W emulsion with a separated oil phase (O/W$_{unstab}$+O), and 4) a two-liquid-phase region plus a solid (O+W+S). It is also clear that the stable O/W emulsion region is affected by the type of CD. Indeed, the region for the stable emulsion phase extends in the following order: α-CD < γ-CD < β-CD. These results can be explained by the variation in the cavity sizes. Indeed, the penetration of the guest molecules into the cavity of CDs was studied by the PM7-DH+ method.[17] From the minimum-energy structures of the complexes shown in Figure S1 in the Supporting Information, it can be explicitly understood that **1** fits the cavity size of β-CD very well contrary to α- (the guest does not deeply penetrate into the cavity) and γ-CD (the cavity is too large to achieve good stabilization of the guest). The calculated binding energies are −71, −94, and −86 kJ mol^{-1} for the inclusion of **1** into the α-, β-, and γ-CDs, respectively, which are in good agreement with the experimental observations. Because optimal complexation is obtained with β-CD, this CD was further investigated. It is noteworthy that, for a given CD percentage in the O/W$_{stab}$ region, the emulsion viscosity increases when the **1**/water ratio increases. Moreover, for a given **1**/water ratio, the emulsion viscosity increases when the amount of CD increases. Finally, the best long-term stability is obtained for high-viscosity emulsions. Therefore, the best compromise between stability and viscosity is obtained for 10 wt % CD supplemented with 45 wt % water and 45 wt % substrate, that is, **1** at a concentration of 4 M. The phase diagrams of the other oil phases investigated [i.e., cycloheptene (**2**), cyclohexene (**3**), 1-methylcyclohexene (**4**), styrene (**5**), diphenylsulfide (**6**), thioanisole (**7**), and dibutylsulfide (**8**)] are presented in the Supporting Information (Figures S2–S9).

The emulsion stability was investigated by multiple light scattering at 60 °C (Figure 4).[18] Because the backscattering intensity is related to the volume fraction of the dispersed phase, local changes in concentration and global changes in size can be detected. As a function of time, we can see a backscattering increase at the bottom of the sample and a decrease at the top of the sample due to a sedimentation process.[15d] Moreover, the evolution over time of the reflectance at mid-height of the tube indicates only a slight increase in droplet size. However, the variation of the diffuse reflectance remains weak and no variation (i.e., phase separation) is visually noticeable after six months. This behavior is characteristic of a slow limited-coalescence process.[19] Although the emulsion exhibits long-term stability, ultimate coalescence can be induced on request by centrifugation (see above).

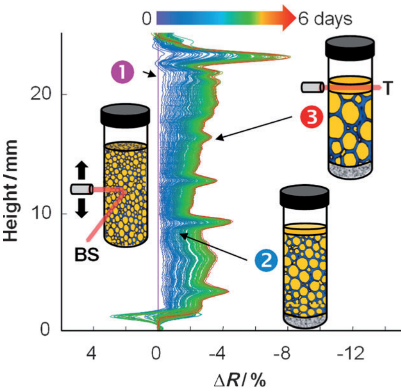
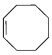
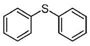
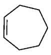
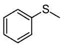
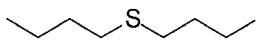
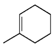
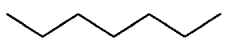
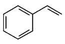
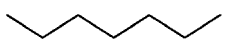


Figure 4. Evolution of the residual diffuse reflectance, ΔR, at 60 °C versus sample height and time for the cyclooctene **1**/water/β-CD contact (45/45/10 wt %, 11 500 rpm, 60 s; T = transmitted light, BS = backscattered light).

The microstructure of the **1**/water emulsion obtained with β-CD was examined by optical microscopy and the droplet size distribution of the stable O/W emulsion was determined; the average droplet size is about 38 μm (Figure 5). Moreover, the birefringence of the droplets under crossed polarization was due the adsorption of CD/**1** ICs on the surface of the droplets.

The scope of the oils was then extended by replacing **1** with other potentially oxidizable liquid substrates, notably alkenes **1**–**5** and sulfides **6**–**8** (see below and Table 1).

Table 1. Average droplet size of Pickering emulsions as a function of the oil phase.[a]

	Oil phase	$D^{[b]}$ [μm]		Oil phase	$D^{[b]}$ [μm]
1		38	**6**		25
2		28	**7**		23
3		33	**8**		27
4		34	**9**		59
5		35	**9**		59

[a] Conditions: oil/water/β-CD (45/45/10 wt %), 11 500 rpm, 60 s. [b] Obtained from ImageJ (N.I.H., USA) and fitting with the log-normal function (standard deviation = 10 %).

The physicochemical properties of the emulsion, which is stabilized by the formation of insoluble ICs between native CDs and the substrates that constitute the oil phase (i.e., O/W interface increase and emulsion stability), combined with its easy breaking by centrifugation make such systems of particular interest for catalytic oxidations involving H_2O_2 as the oxidant and the well-known $[Na]_3[PW_{12}O_{40}]$ water-soluble POM. The optimal conditions for the reaction were determined by using **1** as a model substrate because of its easy and selective conversion into the corresponding epoxide (Table 2). It is noteworthy that the addition of H_2O_2 and catalyst does not disturb the stability of the emulsion system. The addition of H_2O_2 (0.27 equiv) allows a maximal conversion of 27 % of the substrate oil phase. The reactions were performed without stirring.

As a control experiment, the epoxidation at 65 °C in the presence of $[Na]_3[PW_{12}O_{40}]$ and H_2O_2 in a simple biphasic water/**1** system free of β-CD gave no conversion (Table 2, entry 1). This value is typical of POM-catalyzed oxidations without PTC. In the presence of 0.025 mmol of β-CD (i.e., 18.5 mM in water) and $[Na]_3[PW_{12}O_{40}]$, no emulsion and no catalytic activity are obtained (Table 2, entry 2). In contrast, when 0.26 mmol was used, a stable emulsion formed and the conversion reached 24 % after 3 h (Table 2, entries 3 vs. 2). This good activity clearly results from the microstructured reaction medium, that is, emulsion provide a much larger W/O in-

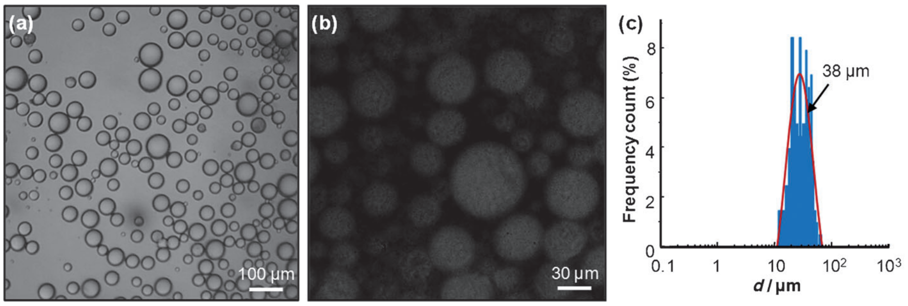


Figure 5. Microphotographs observed after dilution of the O/W emulsion shown in Figure 4 in water (a) and under cross-polarization (b), and the droplet size distribution profile (c).

Table 2. Catalytic epoxidation of **1** with H_2O_2 in unstirred Pickering emulsion systems at 65 °C.[a]

Entry	CD [mmol]	Emulsion	Catalyst	Conv.[b] [%]	TOF_0[c] [h^{-1}]
1	0	no	$Na_3PW_{12}O_{40}$	<1	–
2	0.025	no	$Na_3PW_{12}O_{40}$	<1	–
3	0.26	yes	$Na_3PW_{12}O_{40}$	24	42
4[d]	0.26	yes	$Na_3PW_{12}O_{40}$	49	400
5[e]	1.3	yes	$Na_3PW_{12}O_{40}$	>99	372
6	0.26	yes	$H_3PW_{12}O_{40}$	20	38
7	0.26	yes	$Na_3PW_4O_{24}$	5	7
8[f]	0.26	yes	$Na_3PW_{12}O_{40}$	<1	–

[a] Conditions: 30 μmol of catalyst, 3.5 mmol of H_2O_2, 13 mmol of **1**, 1.35 mL of H_2O, 3 h. [b] Determined by ^{1}H NMR spectroscopy, epoxide >99%. [c] Initial turnover frequency. [d] 11 mmol of H_2O_2, 8 h. [e] Conditions: 30 μmol of catalyst, 6.3 mmol of H_2O_2, 6 mmol of **1**, 1.35 mL of H_2O, 2 mL of heptane, 30 min. [f] 9×10^{-2} mmol of α-tocopherol.

terfacial area (increase of ≈600). Moreover, the apparent activation energy of the **1**/water/β-CD system is estimated to be 25.4 kJ mol^{-1}. This activation energy is lower than that reported for tungsten-catalyzed epoxidation (between 50 and 90 kJ mol^{-1}).[20] This suggests that the process is diffusion controlled. At 65 °C, it is also relevant to note that stirring (750 rpm) has no effect on the catalytic activity, indicating that the viscosity is responsible for the diffusion limitation. In the presence of 0.85 equivalents of H_2O_2 relative to the substrate, the conversion reaches 49% after 8 h and the turnover frequency (TOF_0) is multiplied by about 10 (Table 2, entry 4). The conversion does not reach 85% as expected, probably due to blockage of interfacial active sites by the more polar epoxide, compared with the substrate. This drawback can, however, be overcome if required by replacing the "substrate" oil phase with *n*-heptane. In this case, the catalytic activity increases up to 372 h^{-1} for a conversion of >99% after 0.5 h (Table 2, entry 5). The possibility of using a solvent is also required for solid substrates (see below, in the case of sulfide oxidation). In the presence of $H_3[PW_{12}O_{40}]$, the conversion is less important than that with $[Na]_3[PW_{12}O_{40}]$ (Table 2, entries 6 vs. 3). With $H_3[PW_{12}O_{40}]$, the reaction medium becomes acidic, pH ≈ 1, and under such conditions, at 65 °C, the CD starts to degrade, leading to a decrease of the catalytic activity.[21] Because the $[PW_{12}O_{40}]^{3-}$ anion is known to form the Venturello catalyst, $[PW_4O_{24}]^{3-}$, in the presence of H_2O_2, and thus, acting as a precursor of the active species, $[Na]_3[PW_4O_{24}]$ was also prepared and investigated. Although it allows the formation of a stable emulsion, the replacement of $[PW_{12}O_{40}]^{3-}$ with $[PW_4O_{24}]^{3-}$, surprisingly, provides a much lower catalytic activity in terms of both conversion and TOF_0 (see Table 2, entry 7). Indeed, during the decomposition of $[PW_{12}O_{40}]^{3-}$, several other catalytic species are formed in addition to $[PW_4O_{24}]^{3-}$ (e.g., $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$).[8d] These active $[PW_{12}O_{40}]^{3-}$ decomposition products (i.e., peroxotungstates), which are involved in catalysis, are known to form in trace amounts in an irreversible way. However, it seems that their combination is required because the Venturello species alone exhibits a lower activity. Moreover, in our system with $[Na]_3[PW_{12}O_{40}]$ as a "pre-catalyst", this does not alter the catalysis efficiency because all of these species remain in the aqueous phase due to the absence of cationic PTCs, which is also supported by the recycling of the catalytic system after five consecutive runs (see below). Finally, we noticed that the reaction was completely inhibited when the starting materials contained traces of antioxidants because they are often commercialized. Hence, all substrates were purified or synthesized. Then, to check the involvement of an antioxidant, α-tocopherol (9×10^{-2} mmol) was added to the catalytic system. The finding clearly shows that the reaction does not work at all (compare Table 2, entries 8 and 3). The addition of radical scavengers (i.e., antioxidants) is often used to highlight the formation of radical species during the oxidation process. Moreover, the occurrence of a radical pathway often results in the formation of various byproducts, especially for **3**. Here, the selectivity in epoxide is very high for **3** (>99%; Table 3). Therefore, we believe that another reason to account for the absence of the conversion of **1** when tocopherol is added might be the blockage of active sites by the β-CD/α-tocopherol complex. Indeed, in the presence of β-CD, α-tocopherol competes with the substrate, leading to fat- and water-insoluble ICs.[22] The β-CD/α-tocopherol ICs are located at the **1**/water interface, leading to a reduction in the number of free active sites.[22b] This finding indirectly confirms that the catalytic reaction takes place at the W/O interface (Figure 6).

Table 3. Catalytic epoxidation of olefins in olefin/water emulsion stabilized by β-CD/olefin complexes at 65 °C.[a]

Substrate	Δt [h]	Conversion[b] [%]	Epoxide [%]	TOF_0[c] [h^{-1}]
1	3	24	>99	42
2	3	24	>99	38
3	0.5	24	>99	236
4	3	25	>99	38
5	3	24	43	45

[a] Conditions: 30 μmol of $[Na]_3[PW_{12}O_{40}]$, 3 to 3.5 mmol of H_2O_2, 0.26 mmol of β-CD, 1.35 g of water, 1.35 g of olefin (12 to 14 mmol). [b] Determined by ^{1}H NMR spectroscopy. [c] Initial turnover frequency.

The recycling of the catalytic system was then investigated: the already used emulsified reaction medium was centrifuged (4000 rpm for 5 min) and the upper organic phase was simply removed and new batches of **1** (13 mmol) and H_2O_2 (3.5 mmol) were added to the lower aqueous phase and the particles of ICs. The reaction proceeded without any lost of activity (i.e., conversion and TOF_0) and selectivity after at least five consecutive cycles. These observations are indicative of the stability the particles of ICs under our catalytic conditions (see Figure S10 in the Supporting Information). Moreover, FTIR spectroscopy experiments were performed on the solid CDs after decomplexation with tetrahydrofuran. As depicted in Figure S11 in the Supporting Information, the FTIR spectra were identical before and after five runs. It is noteworthy that, under the conditions described in Table 2, entry 3, the yield of isolated product was 23%, that is, about 1 M.

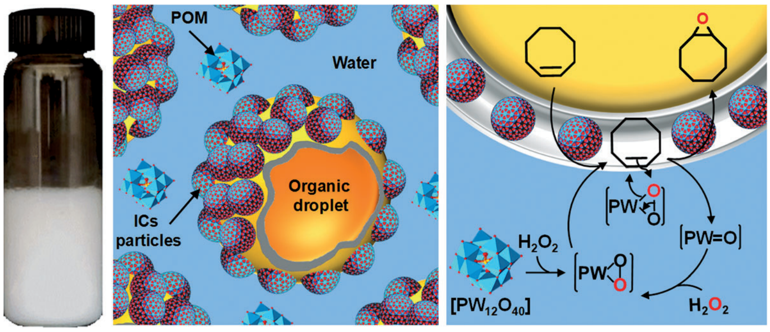


Figure 6. Proposed mechanism for eco-friendly catalytic epoxidation in **1**/water/β-CD Pickering emulsions.

Next, the epoxidation of **2**, **3**, **4**, and **5** was carried out under same reaction conditions (Table 3). It is noteworthy that control experiments, performed without β-CD, gave no conversion after 3 h regardless of the substrate. The reactivities of **2**, **4**, and **5** were similar to that of **1** ($TOF_0 \approx 40\ h^{-1}$) and the reaction was complete within 3 h with 0.27 equivalents of H_2O_2 relative to the substrate. For **3**, a very satisfactory conversion was obtained within only 0.5 h and a clear increase of the kinetic rate was observed ($236\ h^{-1}$). It is noteworthy that the epoxide selectivities were >99 %, except for **5**, for which a significant decrease was observed with time in favor of the corresponding diol. Indeed, this epoxide is more readily hydrolyzed due to the increase of its hydrophilic character and its favored conformation at the interface compared with the epoxycycloalkanes. However, in all cases, the catalytic activities were higher or at least equivalent to that of biphasic reactions performed with PTCs reported in the literature.[8b,d] Under homogeneous conditions with the $H_3[PW_{12}O_{40}]$ catalyst, Maksimchuk et al. reported TOF_0 values of 24.0, 24.6, and 5.4 h^{-1} for the epoxidation of **1**, **3**, and **5**,[23] respectively, versus 42, 236, and 45 h^{-1} reported herein. Moreover, the reaction requires 2 equivalents of H_2O_2 per equivalent of substrate for **1**, **2**, and **5** and the selectivities in epoxides are lower than those obtained with the Pickering emulsion systems, in particular, for substrates **1** and **3**, that is, 95 and 78 %, respectively. On the other hand, Gresley et al. reported on the epoxidation of **2** and **3** with the $[(n\text{-}C_6H_{13})_4N]_3[PW_4O_{24}]$ catalyst in a benzene/water biphasic system under reflux conditions (75 °C).[24] The TOF_0 values are 59.0 and 17.0 h^{-1} for **2** and **3**, respectively. However, although the reactions are very selective in epoxides, the presence of benzene is unacceptable for an industrial process and the catalyst and products cannot be separated easily. In contrast, catalytic solvent-free Pickering emulsions, in addition to their efficiency in terms of catalytic activity, constitute a simple and smart solution for the workup of the final reaction medium.

Fossil fuels, coal, petroleum, and natural gas contain undesirable pollutants (i.e., organosulfurs). Oxidative desulfurization (ODS), based on environmentally friendly oxidizing agents, such as H_2O_2, and combined with a catalytic process, is one of the most promising alternatives to hydrodesulfurization because it generally requires milder conditions and lower operating costs.[25] There have been recent reports on ODS processes involving H_2O_2 and various catalytic POMs.[26] For example, reactions with $H_3[PW_{12}O_{40}]$ proceed in biphasic systems in the presence of cationic PTCs.[27] Li et al. reported an amphiphilic catalyst based on $[(n\text{-}C_{18}H_{37})_2N(CH_3)_2]_3\text{-}[PW_{12}O_{40}]$ assembled in an emulsion in diesel for ODS at 60 °C.[28] This amphiphilic catalyst is effective for selective ODS because it achieves high substrate conversion (>95 %), but the system used, that is, the emulsion, does not allow easy separation of the products and catalyst. When the reaction proceeds rapidly (e.g., 0.5 to 1 h), a large excess of H_2O_2 (≥10 equiv) and/or relatively high temperatures (≥60 °C) are needed, whereas lower H_2O_2 to substrate ratios and/or lower temperatures require longer reaction times (≥5 h).[28,29] Acidic three-liquid-phase microemulsion systems based on tungstate catalytic surfactants can be used to circumvent all these drawbacks.[30]

The catalytic Pickering emulsion described above was also applied to the oxidation of **6**, **7**, **8**, dibenzylsulfide (**10**), and dibenzothiophene (**11**). These substrates are known to oxidize into the corresponding sulfoxide, SO, and/or sulfone, SO_2 (Table 4), although the selective formation of the sulfoxide is still challenging.

Table 4. Catalytic oxidation of organosulfurs (S) into sulfoxides (SO) and/or sulfones (SO_2) in Pickering emulsion stabilized by β-CD/substrates or β-CD/heptane complexes at 65 °C.[a]

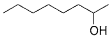
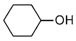
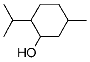
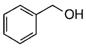
Substrate	Δt [h]	Conversion[b] [%]	Selectivity [%] SO	Selectivity [%] SO_2	TOF_0[c] [h^{-1}]
6	1.5	17 (<1)[d]	75	25	28
7	1	25 (3)[d]	87	13	141
8	3	21 (4)[d]	73	27	42
10[e]	0.5	95 (<1)[d]	83	17	45
11[e]	0.5	96 (<1)[d]	54	46	43

[a] Conditions: 30 μmol of $[Na]_3[PW_{12}O_{40}]$, 2.0 to 3.0 mmol of H_2O_2, 0.26 mmol of β-CD, 1.35 g of water, 1.35 g of organosulfur (6.3 to 10.8 mmol). [b] Determined by ^1H NMR spectroscopy. [c] Initial turnover frequency. [d] Control experiment without β-CD. [e] Conditions: 30 μmol of $[Na]_3[PW_{12}O_{40}]$, 0.95 mmol of H_2O_2, 0.26 mmol of β-CD, 0.67 mmol of organosulfur, 1.35 g of water, 1.35 g of heptane.

Substrates **10** and **11** were oxidized in heptane/β-CD/water emulsions because they were solids. It is noteworthy that without β-CD they gave no or very weak conversion after 3 h. The oxidizing system is particularly efficient for all of the investigated organosulfur compounds. Indeed, as for **6**, **7**, and **8**, more than 17 % of the starting materials are converted into the corresponding sulfoxide and/or sulfone with 0.27 equivalents of H_2O_2 within very short reaction times. Moreover, the catalytic system is very active in the heptane/β-CD/water emulsions with **10** and **11** because conversions are higher than 95 %. In the literature, the prevalence of sulfoxides or sulfones is dictated by the number of equivalents of H_2O_2. Indeed, with substoichiometric amounts of H_2O_2, the sulfoxides are prevalent, whereas the sulfones are obtained with surstoichiometric ratios of H_2O_2 relative to the substrate.[31] Here again, the reactions are particularly efficient in terms of substrate conversion compared with the amount of H_2O_2 added. Moreover, for all of the organosulfur compounds investigated, the reactions performed in the CD-based Pickering emulsions are highly selective to the sulfoxide (>75%), except for **11**.

Finally, to extend the scope of the system to other types of oxidation reactions, in particular, to alcohol oxidations, 2-octanol (**12**), cyclohexanol (**13**), menthol (**14**), and benzyl alcohol (**15**) were also investigated. These substrates were oxidized in heptane/β-CD/water emulsions because using alcohols as the solvent phase did not provide stable Pickering emulsions above 35 °C. The reactions were conducted at 40 °C and the products obtained were the corresponding ketones for **12**, **13**, and **14**, and aldehydes for **15** (Table 5).

Table 5. Catalytic oxidation of alcohols into ketones or aldehydes in Pickering emulsion stabilized by β-CD/heptane complexes at 40 °C.[a]

	Substrate	Conversion[b] [%]	Selectivity [%]
12		>99	>99
13		>99	>99
14		>99	>99
15		44	>99

[a] Conditions: 30 μmol of $[Na]_3[PW_{12}O_{40}]$, 0.85 mmol of H_2O_2, 0.26 mmol of β-CD, 0.67 mmol of alcohol, 1.35 g of water, 1.35 g of heptane, 24 h. [b] Determined by ^1H NMR spectroscopy.

According to reports in the literature, the oxidation of alcohols (**12**, **13**, and **14**) by the $[PW_{12}O_{40}]$ anion in a biphasic system (water/chloroform) is not straightforward.[32] Even although it is easier under homogeneous conditions, a large excess of H_2O_2 (6 equiv), relatively high temperatures (82 °C), and relatively long reaction times are needed to reach a complete conversion of the starting material.[32] Li et al. proposed the use of $[(n\text{-}C_{18}H_{37})N(CH_3)_3]_3[PW_{12}O_{40}]$ as a catalyst for the formation of O/W emulsions.[28b] This system works with a stoichiometric ratio of H_2O_2 relative to the substrate, but complete conversion is reached after 24 h at 80 °C and separation of the emulsion can occur, depending on the nature of the reactants and products.[28b] For almost all of the alcohols investigated (see Table 5), reactions in the CD-based Pickering emulsions are as fast and as selective as those reported in the literature,[8b,32] but proceed at a lower temperature (40 °C), and offer a simple and efficient separation method. Indeed, unlike the emulsions based on olefins or sulfides described above, the CD-based emulsions containing alcohols or their corresponding oxidation products, that is, aldehydes and ketones, are thermosensitive and provide an additional benefit because they can be readily destabilized at the end of the reaction by heating instead of centrifugation. Thus a compromise must be found between the reaction temperature, which must ensure the stability of the emulsion system during the process and good conversion of the starting substrate, and the temperature causing the separation of the emulsion on request at the end of the reaction, which must allow good separation of the emulsion for easy workup and recycling of the reaction medium. For the alcohols **12**–**15**, 40 and 65 °C are good compromises to ensure the stability associated with good catalytic efficiency and the separation of the emulsion, respectively. It is finally noteworthy that, as described in the literature, the oxidation of **15** is often difficult to achieve because the alcohol is primary.[33] However, in the CD-based Pickering emulsion we obtain a very good aldehyde selectivity, that is, no other oxidation products; this is contrary to that reported in the literature data.[34]

Conclusions

We explored and widened the scope of the solventless catalytic Pickering emulsion concept: a biphasic mixture of various liquid substrates and water formed emulsions in the presence of CDs through the formation of amphiphilic insoluble ICs with the substrate. Such emulsions, in combination with the $[Na]_3[PW_{12}O_{40}]$ catalyst, were highly efficient reaction media for the oxidation of olefins, organosulfurs, and alcohols, leading to competitive rates, good yields, and selectivities. Such catalytic emulsions combine the advantages of biphasic catalysis, without the drawbacks (e.g., separation time or catalyst leaching), and heterogeneous catalysis because they allow easy separation of the products and catalysts by simple centrifugation or heating. In comparison with immobilization on silica, this catalytic system did not require synthetic steps. Moreover, the proposed system is versatile, depending on the nature of the substrate (solid or liquid) and it is eco-friendly because it does not require any organic solvent, except when the substrate is solid, nor a PTC and does not generate waste. Due to current interest in new catalytic processes, further developments of these catalytic Pickering emulsions are expected for other catalytic processes.

Experimental Section

General information: $[D_6]$DMSO and all other chemicals were purchased from Aldrich. Distilled deionized water was used in all experiments. All solvents and liquid reagents were degassed by bubbling nitrogen for 15 min before each use or by two freeze–pump–thaw cycles before use. All reactions were performed in oven-dried glassware under nitrogen by using standard Schlenk and vacuum-line techniques. All measurements were taken in a thermostated water bath. The temperature stabilization was estimated to be better than ±0.05 °C with a thermoregulated bath Lauda RC6. All emulsifications were performed by using an Ultra-Turrax instrument (11 500 rpm, IKA, T 10 basic).

NMR spectroscopic characterization: The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded by using an Advance 300 Bruker spectrometer at 300.13, 75.49, and 121.49 MHz, respectively. Chemical shifts are given in ppm (δ) and measured relative to residual solvent, for ^1H and ^{13}C NMR spectroscopy, and to an external reference (H_3PO_4) for $^{31}P\{^1H\}$ NMR spectroscopy.

FTIR characterization: IR analyses were performed with a FTIR spectrometer PARAGON 500 (Perkin–Elmer) using KBr wafers containing 5 wt% of product by 64 scans with a resolution of 1 cm^{-1}.

Particle characterization: The nanoparticles were examined by using a Philips CM30 transmission electron microscope. Before analysis, the powders were dispersed in water. Two drops of water containing the nanoparticles were then deposited on a carbon–copper grid (13 mm radius).

Emulsion characterization: Microphotographs were obtained by using a light microscope (Standard 25 ICS, Zeiss) coupled with a charge-coupled device (CCD) Camera (Digital Still Camera, SONY). Images were analyzed with ImageJ software (National Institutes of Health, USA) to obtain the size of the droplets. The distribution function was obtained by treatment of experimental data with a log-normal function (OriginPro 8, USA). The emulsion stability was measured at constant temperature (25 °C) by multiple light scattering using a Turbiscan Lab Expert (Formulaction).

Synthesis of $[Na]_3[PW_4O_{24}]$: Tungstic acid (2.5 g, 10 mmol) was treated with 50% hydrogen peroxide (4.2 mL, 70 mmol). After 20 min reaction at 50 °C and then filtration, H_3PO_4 solution (1 mL, 2.54 mmol) was added. The solution was stirred for 10 min and an aqueous solution of NaOH (3.3 mmol) was added dropwise to the system until neutralization. Yield: 91%; $^{31}P\{^1H\}$ NMR (121 MHz, $[D_6]$DMSO, 20 °C): $\delta = 1.7$ ppm (d, $^2J(W,P) = 18.4$ Hz).

General biphasic oxidation experiments: $[Na]_3[PW_{12}O_{40}]$ (30.0 μmol) and H_2O_2 (6 mmol) were dissolved in water (1.35 g). β-CD (264 μmol) was mixed with the substrate (olefin or sulfide, 1.35 g). The two solutions were charged into a 10 mL reactor, which was emulsified by using an Ultra-Turrax instrument (11 500 rpm, IKA, T 10 basic). The reactor was sealed and heated at 65 °C without stirring. The reaction medium was sampled during the reaction for ^1H NMR spectroscopic analyses. The results presented were the average of at least three runs under each set of conditions.

Acknowledgements

We are most grateful to ANR Catasurf (Project ANR-10-CD2I-01) for financial support, Ahmed Addad for performing TEM experiments, and Wacker Chemical Corp. (Adrian, Michigan, USA) for the generous gift of α-CD.

Keywords: cyclodextrins · nanoparticles · oxidation · Pickering emulsions · polyoxometalates

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Received: January 24, 2013