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Biphasic Catalysis

Pickering Interfacial Catalysis for Biphasic Systems: From Emulsion Design to Green Reactions

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biphasic catalysis · green chemistry · interfaces · phase-transfer catalysis · supported catalysts

Pickering emulsions are surfactant-free dispersions of two immiscible fluids that are kinetically stabilized by colloidal particles. For ecological reasons, these systems have undergone a resurgence of interest to mitigate the use of synthetic surfactants and solvents. Moreover, the use of colloidal particles as stabilizers provides emulsions with original properties compared to surfactant-stabilized emulsions, microemulsions, and micellar systems. Despite these specific advantages, the application of Pickering emulsions to catalysis has been rarely explored. This Minireview describes very recent examples of hybrid and composite amphiphilic materials for the design of interfacial catalysts in Pickering emulsions with special emphasis on their assets and challenges for industrially relevant biphasic reactions in fine chemistry, biofuel upgrading, and depollution.

1. Introduction

The past two decades have seen the advent of Green Chemistry as a distinctive field within synthetic chemistry aimed at a “smart” (re)design of chemical processes to moderate their environmental impact in an economically beneficial manner. To improve the greenness of a process, three main goals are usually addressed: 1) minimization of the amount of by-products and waste, 2) use of benign reactants and solvents (if possible no solvent), and 3) use of selective catalysts. Most often, it is difficult to reconcile all these principles in a single process. This is especially true for reactions involving biomass-derived reagents, where low reactivity resulting from poor reagent miscibility is the general rule.[1] Nonetheless, such systems constitute a hotbed for innovation, thus opening an avenue to high-value fine chemicals and biofuels that can only be afforded today either by using inefficient processes or for which simply no technological solution exists (Figure 1).

Organic solvents are classically employed in chemical synthesis to boost the solubility/miscibility of the reagents, act as thermal buffers for exothermic reactions, or condition the catalyst efficiency and concentration. Convenient solvents can also favor the separation of the reaction products and catalyst recovery.[2] However, the use of solvents artificially increases the complexity of a reaction system and requires further extraction/purification steps for recovery and recycling. As a matter of fact, about 6.4 Mt of alcohol-based solvents were used worldwide in 2011.[3] Solvents (including water) contribute to 80 % of the mass utilization and 50 % of the energy employed in chemical transformations, and their consumption is expected to grow steadily at an annual rate of 2.5 % until 2019.[3] Accordingly, the design of solvent-free systems appears as an urgent need. With this view, the implementation of green solvents (e.g., water, glycerol and derivatives, ethyl lactate, 2-methyl-substituted THF, D-limonene) for current industrial processes can be visualized as a midterm step in the progress to, ultimately, solvent-free systems.[4]

The development of solvent-free reactions is a challenging task. Liquid–liquid reactions (both homogeneously and

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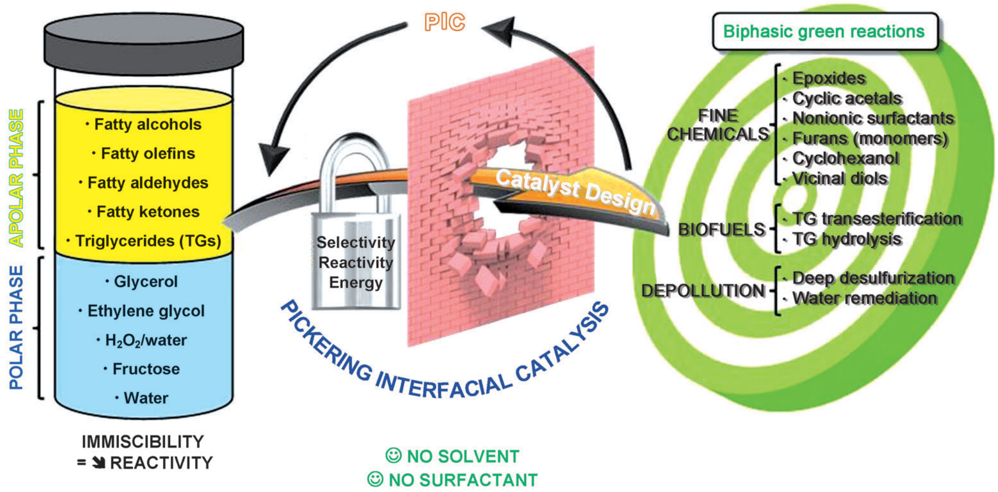

Figure 1. Examples of accessible high-value products and biofuels from ideal reactions involving immiscible biomass-derived reagents.

heterogeneously catalyzed) are commonly carried out in mechanically stirred tank reactors operating in batch, semi-batch, or continuous mode.[5] One of the main drawbacks of stirred reactors is inhomogeneous mixing, which results in resilient-mass/heat-transfer limitations ascribed to a modest interfacial contact, even under vigorous stirring. Surfactants are often required to promote the liquid–liquid (L/L) contact and distribute the catalyst between the phases. However, surfactants increase the environmental impact and carbon footprint of the process. Alternatively, although flow chemistry using microfluidic reactors can promote the contact between immiscible phases at moderate energy supply, industry is still reluctant to its implementation, especially when handling solids (i.e., heterogeneous catalysts).[6]

Given the aforementioned shortcomings of current technologies, the design of the catalyst contact near the L–L interface is mandatory. In this Minireview, we provide a critical assessment of systems operating by interfacial

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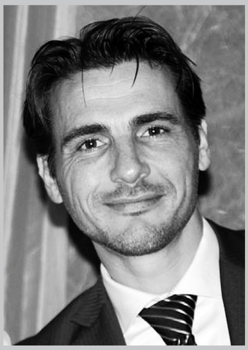

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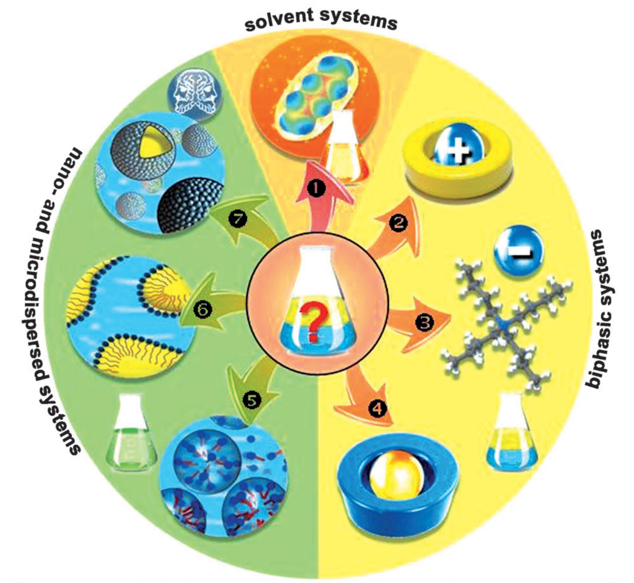
catalysis in Pickering emulsions (or simply Pickering interfacial catalysis; PIC), which constitutes a novel and versatile field with promising green credentials for solvent-free biphasic reactions. To guide the reader, the first section offers a description of biphasic systems and a systematic classification of recent concepts which can be exploited, with variable degrees of success, for preventing the use of solvents and boosting the reactivity of immiscible reagents. This section is followed by two short sections on surfactant interfacial catalysis (SIC) and Pickering-assisted catalysis (PAC). These systems illustrate the natural transition from surfactant-combined catalysts stabilizing emulsions (SIC) and amphiphilic nanoparticles stabilizing Pickering emulsions combined with a homogeneous catalyst (PAC), to the ultimate generation of intrinsically catalytic amphiphilic nanoparticles encompassing Pickering emulsions (PIC).



❶ single or mixed solvents; ❷ and ❸ normal phase-transfer catalysis by crown ethers and onium salts (NPTC); ❹ inverse phase-transfer catalysis by cyclodextrins (IPTC); ❺ micellar catalysis (MC); ❻ microemulsion catalysis (MEC); ❼ Pickering emulsion catalysis (PEC): Pickering assisted catalysis (PAC) + Pickering interfacial catalysis (PIC)

Figure 2. Main concepts for boosting catalysis in biphasic systems.

2. Biphasic Systems: Main Concepts

Before starting our immersion into PIC systems, let us concentrate on different concepts that have appeared in the last years covering biphasic systems and catalysis. Such concepts usually entail water-in-oil (w/o) or oil-in-water (o/w) systems to afford organic syntheses in water. However, their extrapolation to solvent-free systems is sometimes intricate. The purpose of this section is to disentangle these different concepts and classical borders, and unveil the potentials and limitations for carrying out reactions with immiscible reagents. A tentative classification is proposed relying on the dispersion type (i.e., biphasic systems, micelles, microemulsions, and emulsions), the nature of the surface-active or phase-transfer agent, and location of the catalyst in the L–L system (Table 1 and Figure 2). This classification is by far not exhaustive and examples of hybrid systems sharing common properties appear frequently. Note also that examples of systems with undefined or biased catalytic mechanisms are common, especially when combining surfactants and homogeneous catalysts. In such a situation, it is sometimes arduous to predict the phase partition of the catalyst, as well as the actual role of the L–L interface in the catalytic process. In the latter case, the dichotomy of interfacial versus bulk catalysis is recurrent.

2.1. Phase-Transfer Catalysis (PTC)

Normal phase-transfer catalysis (NPTC)[7] typically employs quaternary ammonium and phosphonium salts or crown ethers, which are soluble in both aqueous and organic phases, thus promoting reactions (often catalyzed by an additional homogeneous catalyst) by the preferential transfer of reactants from the aqueous to the organic phase, but without formation of an emulsion. A related concept is the inverse phase-transfer catalysis (IPTC) which utilizes cyclodextrins (CDs) and calixarenes, as they are able to solubilize organic compounds in aqueous solutions through the formation of inclusion complexes.[8] Calixarenes incorporating acid groups can also combine phase-transfer and interfacial catalytic effects.[9] In a similar manner, phase-boundary catalysis (PBC) uses amphiphilic solid nanoparticles (usually zeolites) lying at the boundary between the aqueous and organic phases, but with no formation of Pickering emulsions.[10] NPTC and IPTC are mature technologies, which are usually restricted to w/o systems and offer poor catalyst recyclability. It is noteworthy that the PTC concept can be extended to supported PTC systems.[11] In some cases, phase-transfer catalysts can be used directly as ionic liquids.[12]

2.2. Micellar Catalysis (MC)

This term refers to the dispersion of two immiscible phases by the generation of amphiphilic supramolecular assemblies, that is, micelles (object size 5–10 nm), using surfactants. Preferential solubilization of liphophilic reagents occurs in the hydrophobic micelle core, leading to a higher reagent concentration than that in the surrounding water, and to potential synergistic hydrophobic effects with the surfactant (e.g., stabilization of transition complexes). MC covers three systems depending on the location of the catalyst: a) Micellar inverse phase-transfer catalysis (MIPTC), where the liphophilic substrate is transferred into an aqueous phase and the reaction takes place at the surface of the micelles in the water phase;[2,13] b) micellar-assisted catalysis (MAC), where an homogeneous catalyst is mainly located in one of the phases (most often confined inside the micelles);[14] and c) micellar interfacial catalysis (MIC), where the catalyst is either located at the w/o interface together with the surfactant, or consists of a surfactant-combined catalyst at the

Table 1: Summary of concepts appeared in the literature for catalysis in biphasic systems.

System			Concept	Surface-active or phase-transfer agent	Catalyst location
biphasic (demixed system)	phase-transfer catalysis (PTC)		normal phase-transfer catalysis (NPTC)	onium salts, crown ethers (both phases)	one or both phases
			inverse phase-transfer catalysis (IPTC)	cyclodextrins, calixarenes (both phases)	one or both phases
			phase-boundary catalysis (PBC)	amphiphilic zeolites	L/L interface
nanodispersed (5–100 nm)	micellar catalysis (MC)		micellar inverse phase-transfer catalysis (MIPTC)	cationic surfactants	L/L interface
			micellar-assisted catalysis (MAC)	surfactants (normal or reverse micelles)	one or both phases
			micellar interfacial catalysis (MIC)	surfactants (normal or reverse micelles) surfactant-combined catalysts	L/L interface L/L interface
	microemulsion catalysis (MEC)		microemulsion inverse phase-transfer catalysis (MEIPTC)	cationic surfactants, crown ethers	one or both phases
			microemulsion-assisted catalysis (MEAC)	surfactants	one or both phases
			microemulsion interfacial catalysis (MEIC)	surfactants	L/L interface
microdispersed (0.5–200 μm)	emulsion catalysis (EC)	surfactant emulsion catalysis (SEC)	surfactant-assisted catalysis (SAC)	surfactants or polymers	one or both phases
			surfactant interfacial catalysis (SIC)surfactants	L/L interface surfactant-combined catalysts	L/L interface
		Pickering emulsion catalysis (PEC)	Pickering-assisted catalysis (PAC)	amphiphilic nanoparticles	one or both phases
			Pickering interfacial catalysis (PIC)	catalytic amphiphilic nanoparticles catalytic nanohybrids	L/L interface L/L interface

micelle interface (e.g., metal dodecyl sulfates M[DS]$_n$, cetyltrimethylammonium (CTA)–heteropolyacids, amphiphilic enzymes, enzyme–surfactant systems).[14,15] In the latter two systems, the reaction is accelerated by the higher concentration of reagents inside the micelles. In general terms, MC is often limited to low reagent loading and offers low catalyst recyclability.

2.3. Microemulsion Catalysis (MEC)

This concept is similar to MC, but involves the formation of swollen micelles, leading to the microemulsions (μems) with larger aggregate sizes (10-100 nm). In analogy to MC, three concepts encompassing μems can be distinguished: a) Microemulsion inverse phase-transfer catalysis (MEIPTC), where a lipophilic reagent is confined inside the oil-μem droplets;[16] b) Microemulsion-assisted catalysis (MEAC), where an homogeneous catalyst is mainly located inside the water-μem droplets; and c) Microemulsion interfacial catalysis (MEIC) using surfactants that incorporate at least one catalytic function, that is, surfactant-combined catalysts.

A typical example of a MEIC system is dodecylbenzene sulfonic acid (DBSA), which behaves simultaneously as a surfactant and Brønsted acidic catalyst favoring esterification and etherification in water/alkane μems.[17] Unlike conventional acids, DBSA μems can provide a superior reaction medium with higher activity and controllable regioselectivity, even at low temperatures. Furthermore, the generated water can easily be displaced from the reaction zone, thus shifting the equilibrium towards the product. Despite these benefits, MEC has the same drawbacks as MC systems in terms of product and catalyst recovery, and is limited to w/o and o/w systems requiring relatively high amounts of surfactants, unless multiphase μems are used.[18]

2.4. Emulsion Catalysis (EC)

Sharing the common features of MC and MEC, EC relies on the formation of emulsions with droplet sizes within the range 0.5–200 μm. Most often, w/o and o/w emulsions are stabilized by surfactants in combination with a homogeneous catalyst, which is located mostly within the emulsion droplets (i.e., surfactant-assisted catalysis; SAC). However, some surfactant-combined catalysts can promote interfacial catalysis (i.e., surfactant interfacial catalysis; SIC).[19] Kobayashi and co-workers were among the first authors to perform acid-catalyzed reactions in the presence of water using surfactant-combined Brønsted and Lewis acidic catalysts (i.e., DBSA and Sc/Cu dodecyl sulfates and dodecanesulfonates).[20] Moreover, organocatalytic surfactants, most often based on proline and imidazole residues, have also demonstrated high activity, in particular for aldol condensations in emulsion.[21] Key to these reactions is their interfacial nature endowing potential "on-water" effects in emulsion driven by a subtle panel of hydrogen bonds between water and the reactants at the o/w interface.[22] An interplay between in-water and on-water reactions can be used in the engineering of domino/cascade reactions for chemical synthesis, where water can serve as reaction medium, product partitioner, and reaction catalyst.[23]

In addition to surfactants, amphiphilic nanoparticles can also stabilize emulsions (Pickering emulsions), thus offering a platform for the design of efficient catalytic systems.[24] The use of colloidal particles as stabilizers provides w/o and o/w emulsions (and in few cases μems[25]) with original properties compared to surfactant-stabilized emulsions and μems. Indeed, monodisperse emulsions with a controlled size at the micrometer to millimeter range can be easily generated by taking advantage of the "limited coalescence" process. In the simplest approach, a homogeneous catalyst can be combined with a Pickering emulsifier located either in the dispersed or continuous phases. For the sake of clarity, this concept is termed here as Pickering-assisted catalysis (PAC).

As an ultimate evolution of MIC, MEIC, and PAC systems, the PIC concept aims at the generation of stable Pickering emulsions between immiscible reagents by adsorbing at the w/o interface amphiphilic particles bearing catalytic groups and showing easy recyclability. This concept is expected to open an avenue to the design of cascade reactions by promoting phase-selective catalysis for the synthesis of complex molecules with neither need of solvent nor protection of vulnerable functional groups.[26]

3. Surfactant-Combined catalysts in MIC, MEIC, and SIC Systems

This section deals with catalytic surfactants behaving simultaneously as emulsifiers and interfacial catalysts for biphasic reactions. In such systems, the generation of an interfacial surface (about 1000 times compared to a classical biphasic system), ascribed to the formation of stable microdroplets, promotes mass transfer of reagents between two different phases, and in turn the reactivity. Within this general framework, the different catalytic systems can be broadly classified into four families depending on the nature of the catalytic sites. Given the importance of the reported systems, only the most significant and illustrative examples are herein described.

3.1. Amphiphilic Acid/Base Catalysts

In 2007, Gang et al. published the first successful solvent-free esterification reaction catalyzed by Brønsted and Lewis acidic surfactant-combined catalysts (DBSA and [Cu-$(DBS)_2$]; DBS = dodecylbenzenesulfonate).[27] Reversible micelles were generated that promoted the extraction of the generated water while the reaction was concomitantly catalyzed at near room temperature (MIC system). More recently, Ghesti et al. reported additional examples of cerium and other rare-earth DS catalysts for the transesterification of soybean oil with methanol and ethanol, operating by the formation of micelles (MIC systems).[28] The soybean oil conversion achieved values of higher than 95% at 100°C for $[Ce(DS)_3]$. However, the catalytic activity decreased in the order Ce > Sm > Gd > La, which was attributed to a higher catalyst deactivation.

In addition to MIC systems, some examples of SIC systems have appeared in the literature. In 2011, Jérôme and co-workers reported the direct etherification of glycerol with long-chain alcohols ($>C_6$) in biphasic conditions.[29] DBSA was used for promoting the emulsification of the reaction medium (Figure 3), which resulted in the formation of monododecyl glyceryl ether with a 30% yield. In 2012, He et al. prepared fatty phytostanyl laurate, a cholesterol-lowering food additive, by the esterification reaction of phytosterols with lauric acid in the presence of DS and HCl.[30] The authors reported a yield as high as 92% after optimization of the reaction parameters. Later on, the same team extended the preparation of phytostanyl laurate to copper and cerium dodecyl sulfates (i.e., $[Cu(DS)_2]$ and $[Ce(DS)_3]$, respectively) as Lewis acidic surfactant-combined catalysts, which showed in all cases promising activities.[31]

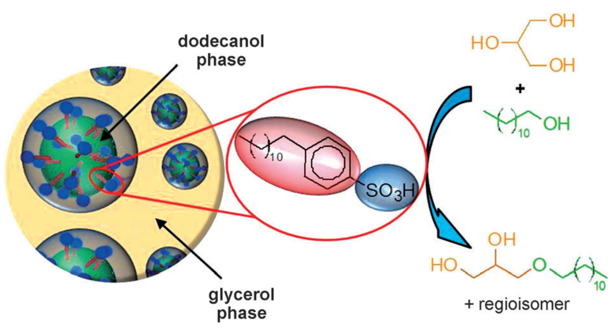


Figure 3. Principle of DBSA catalytic surfactant to perform interfacial etherification catalysis in a reverse microemulsion.

In 2012, Hou and co-workers reported a similar surfactant-combined catalyst, but based on a room-temperature ionic liquid consisting of a polyoxometalate (POM) anion and triblock copolymer (P123)-functionalized imidazolium cation.[32] The hybrid acid catalyst was found to be highly efficient in the water-free esterification of lauryl alcohol with acetic acid. The alcohol conversion reached a value as high as 90% at 60°C after 5 hours of reaction. The high catalytic activity was attributed to the formation of an emulsion with the droplet size increasing during the reaction. Finally, a thermodynamically unstable emulsion was generated, leading to a catalyst self-precipitation at the end of the reaction.

Recently, temperature-sensitive Brønsted acidic amphiphilic imidazolium salts bearing alkane sulfonic acid and ethylene oxide (EO) groups (Figure 4) were designed to perform the water-free esterification of oleic acid with methanol, affording the synthesis of biodiesel.[33] The catalytic activity was close to that of sulfuric acid and was affected by the number of EO groups, thereby conditioning the hydrophilic/lipophilic balance of the salt and in turn its capacity to

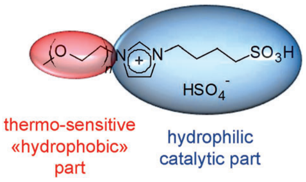


Figure 4. Thermosensitive amphiphilic Brønsted acidic imidazolium salts used for the synthesis of biodiesel.

generate stable acid/alcohol emulsions (SIC system). Indeed, a large number of EO units enhanced the hydrophilic properties, discouraging the formation of stable emulsions, whereas at a lower number of EO units, the catalyst became lipophilic, especially at higher temperatures. This fact combined with the hydrophilic nature of the alkane sulfonic acid group promoted the emulsification with an optimum catalytic performance for $EO = 350$. Notably, contrary to homogeneous catalytic systems, the produced biodiesel could be separated by simple decantation and the catalyst could be reused up to five times.

In addition to Brønsted and Lewis acidic catalysts, Nawaratna et al. recently described the only example of a surfactant-combined basic catalyst for the transesterification of triglycerides with alcohols.[34] This catalyst was built as an assembly of amphiphilic titanium alkoxide oligomers incorporating alkyl groups and basic centers, thus favoring the formation of stable triglyceride/alcohol emulsions. The catalytic activity was a strong function of the alkyl chain length, decreasing when the number of carbon atoms in the tail group became longer because of a decline of the basic strength, even if emulsification was favored. The maximum ester yield was about 64 % for titanium methoxide after 3 hours of reaction.

3.2. Amphiphilic Oxidation Catalysts

Molybdate and tungstate anions are classical homogeneous oxidation catalysts. Indeed, in the presence of H_2O_2 and depending on the pH, singlet oxygen ($^1O_2$) or peroxometalates can be generated. However, with Na_2MoO_4 or Na_2WO_4, the oxidation of hydrophobic substrates by H_2O_2 occurs under biphasic conditions and the conversion remains weak. Indeed, $^1O_2$ generated in the aqueous phase from the efficient H_2O_2/MoO_4^{2-} system (yield = 100 %) is rapidly deactivated by water molecules before reaching the substrate in the organic phase ($^1O_2$ lifetime in $H_2O \approx 3\ \mu s$). For Na_2WO_4, which is a better epoxidation catalyst in acid medium, the conversion depends on the solubility of the peroxo species in the organic phase. To promote mass transfer and the w/o interfacial area, cationic surfactants can be used as counterions. By designing well-balanced catalytic surfactants (i.e., packing parameter close to 1), three-liquid-phase μems can spontaneously form at room temperature in the presence of water and an appropriate solvent (i.e., MEIC system).[18] For example, Aubry and co-workers designed a series of balanced catalytic surfactants based on amphiphilic double-tailed quaternary ammonium chains (e.g., dimethyldioctyl) with molybdate as a counterion for the peroxidation of organic substrates in a three-liquid-phase μem in the presence of toluene or propyl acetate.[18a] The reactions proceeded at competitive rates, even with poorly reactive substrates, with easy product separation.

Likewise, three-liquid-phase MEIC systems based on dodecyldimethylammonium tungstate/water/organic solvent and dimethyldioctylammonium (DiC_8) acid salts (dihydrogen phosphate and hydrogen sulfate) have been reported for epoxidation and sulfide oxidation reactions under mild reaction conditions. For instance, Nardello-Rataj and coworkers reported a high catalytic activity and selectivity in the epoxidation of alkenes with H_2O_2 in the presence of $[DiC_{10}]_2WO_4$, $[DiC_8]H_2PO_4$, and $[DiC_8]HSO_4$ in a triphasic μem system based on toluene and water at 50 °C.[18b] The authors attributed the high catalytic performance not only to the nanostructured reaction medium, which favored the compartmentalization and interfacial transfer of reactants and products, and in turn suppressed diol formation, but also to the acid medium mainly obtained with $[DiC_8]HSO_4$ (pH 2–3). In combination with $[DiC_8]H_2PO_4$, this medium allowed the generation of several oxodiperoxo complexes in the presence of H_2O_2 (Venturello complex, $[PO_4\{WO(O_2)_2\}_4]^{3-}$). The Venturello complex can also be generated by the decomposition of tungsten POMs upon treatment with H_2O_2.[35]

POMs are anionic clusters generally soluble in the aqueous phase, but showing low affinity for organic reagents. To counter-balance the POM-anion hydrophilicity and enhance the w/o interfacial area, intrinsically amphiphilic POMs have been prepared, allowing the formation of stable emulsions. Two main strategies have been explored to increase the hydrophobic properties of POMs. The first strategy encompasses the preparation of POM anions noncovalently bound to one or more cationic surfactant(s). The self-assembled catalysts become uniformly distributed at the interface of emulsion droplets and behave as homogeneous catalysts (SIC system). By using such an approach, Li and coworkers reported, in 2004, a $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{16}]$ catalyst to perform cyclohexene expoxidation with H_2O_2 in a biphasic medium ($H_2O/CHCl_3$).[36] The catalytic mechanism involved the degradation of the catalyst into smaller species (e.g., $[(PO_4)\{WO(O_2)_2\}_4]^{3-}$, $[(PO_4)\{WO(O_2)_2(H_2O)\}]^{3-}$, and $[(PO_3(OH))\{WO(O_2)_2\}_2]^{2-}$) which are soluble in $CHCl_3$. Then the active oxygen in the $[W_2O_2(O_2)_4]$ unit reacted with the olefin to form the epoxide. In such a configuration, the system could behave as a SIC or SAC system depending on the location of the catalyst relative to the w/o interface. At the end of the reaction (i.e., after complete H_2O_2 consumption), the initial POM compound was regenerated and precipitated from the reaction solution. Further investigations by the same team on the emulsification properties of various $Q_3[PW_{12}O_{40}]$ (Q = quaternary ammonium cations) systems revealed that, depending on the structure of Q, stable emulsions could be obtained by interfacial assembly.[37] In particular, $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ exhibited a remarkable selectivity and activity in the oxidation of sulfur-containing molecules to sulfones in real diesel and in the oxidation of alcohols to ketones using H_2O_2 as oxidant, because of the formation of a stable emulsion during the reaction. The catalyst could be separated and recycled after demulsification using centrifugation. In addition to the aforementioned studies, Zhu et al. also proposed a possible catalytic mechanism for biphasic oxidation in emulsion by relying on a complete collection of Raman spectra of tungsten and molybdenum peroxo species.[38] The authors suggested a possible conversion of the dimeric $Q_2[M_2O_3(O_2)_4]$ species into monomeric $Q[M(O_2)]$ and H^+ in the presence of excess H_2O_2 (M = W or Mo). In this approach, the detached $Q[M(O_2)]$ species is expected to enter the organic phase and transfer the active oxygen to the substrate, thus affording the oxidation of cyclohexene to adipic acid. Then, the reduced species Q[M(O)] might return to the aqueous phase and be reoxidized to Q[M(O_2)] with H_2O_2, closing the catalytic cycle. The versatility and ease of the assembly between cationic surfactants and anionic catalysts to generate tunable processes have resulted in outstanding developments in oxidation/epoxidation reactions, allowing easy product separation and catalyst recovery.[38,39]

The second strategy relies on the synthesis of organic–inorganic hybrid amphiphilic surfactants where the POM acts as a polar head group. By using such an approach, Liu et al. grafted hexavanadate POM anions with long-chain alkyl tails to obtain POM–organic compounds to afford w/o emulsions (SIC system).[40] The authors applied these systems to desulfurization reactions (Figure 5). Indeed, the conversion rate in thiophene oxidation was significantly enhanced because of the improved contact between the catalyst and the reactants at the w/o interface. The pH value had an influence both on the size and on the nature of emulsions. In a former study from 2008, Kobayashi and Nagano reported a similar concept, using a surfactant-type iron(III) complex, that is, [$Fe_2O(DS)_4$], as an organic–inorganic amphiphilic surfactant for the oxidation of simple aryl alkanes using aqueous *tert*-butylhydroperoxide (TBHP) as an oxidant.[41]

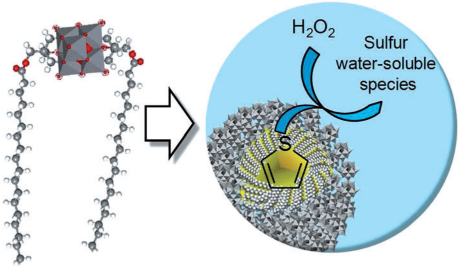


Figure 5. Molecular structure of hexavanadate-based hybrid surfactants used as catalysts for desulfurization.

3.3. Amphiphilic Organometallic Catalysts

Most aldehydes are synthesized by hydroformylation, allowing the synthesis of alcohols after a hydrogenation step. In this context, some authors have explored the use of amphiphilic organometallic complexes in emulsion, thus affording SIC systems. In 2008, Li and co-workers reported the hydrogenation of aldehydes with an amphiphilic polymer-based iridium catalyst affording the emulsification of aldehydes and water (SIC system, Figure 6).[42] This smart system allowed the transfer hydrogenation of aldehydes in water with increased reaction rates as a consequence of the high surface area of the emulsion droplets and the high local concentration of reactants around the active sites.

An attractive example of a CD/surfactant system was reported by Schmitzer et al. to perform interfacial organometallic catalysis in emulsion (SIC system, Figure 7).[43] The authors used cationic surfactants combined with α-CD as a control element in the thermoregulated aqueous rhodium-catalyzed hydroformylation of higher alkenes. Indeed, anionic ligands (e.g., trisulfonated triphenylphosphine) increased the conversion because of rhodium sequestration by the surfactant at the surface of the oil droplet. Moreover, complexation of surfactant unimers into α-CD was favored at 20 °C, whereas the complexes were dissociated during the reaction (80 °C). These complexes enabled the emulsification of the reaction medium driven by surfactant self-assembly. At the end of the reaction, the α-CD helped to break the emulsion by adsorbing the hydrophobic moiety of the surfactant in its cavity, which resulted in a fast decantation process.

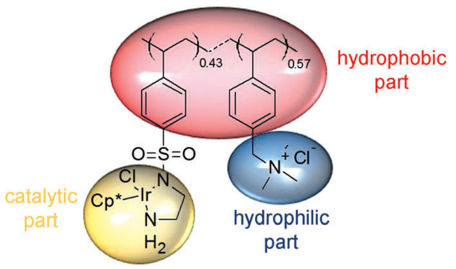


Figure 6. Amphiphilic polymer-based iridium catalyst used for transfer hydrogenation of aldehydes.

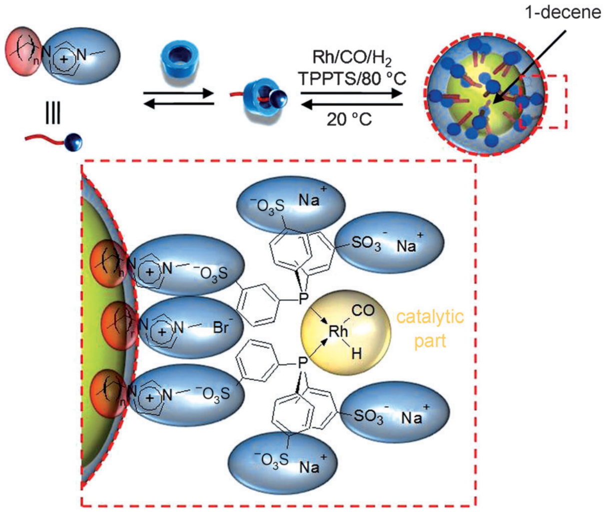


Figure 7. Principle of CD/cationic surfactant combination to perform interfacial catalysis in thermoregulated emulsion. Bottom: a possible active rhodium species during hydroformylation reaction. TPPTS: 3,3′,3′′-Phosphanetriyltris(benzenesulfonic acid) trisodium salt.

Another interesting system was proposed in 2012 by Monflier and co-workers.[44] The authors developed a water-soluble phosphane which was able to self-assemble, rendering micelles (MIC system). Neutral and ionic β-CDs induced contrasting behaviors in this system. In the micellar region, neutral β-CDs formed a complex with the phosphane and destroyed the micelles. In contrast, micelles remained stable with ionic β-CD in a large concentration range. In that case, micelle destruction was only observed with a large excess of ionic β-CD. The catalytic performance of such micellar systems was assessed in the rhodium-catalyzed hydroformylation reaction of 1-decene. The catalytic activity could be improved without a detrimental impact of the ionic β-CD on the regioselectivity. Furthermore, a beneficial effect on the decantation process at the end of the reaction was also reported.

3.4. Enzymes Located at the L/L Interface

Enzymes are highly selective biocatalysts that greatly accelerate both the rate and the specificity of metabolic reactions which sustain life. Enzymes are used to perform organic transformations with superior reaction rates and selectivities compared to classical catalysts. As many substrates are poorly water-soluble, while enzymes naturally require aqueous environments, some authors have attempted the use of enzymes in biphasic aqueous–organic systems.[45]

In this context, examples of lipases favoring the interfacial hydrolysis of triglycerides in w/o emulsions have been reported. Most studies deal with the immobilization of the lipases at the w/o interface assisted by surfactants.[15d,46] A remarkable exception has been reported by Drioli and co-workers.[47] These authors described the distribution of lipases at the w/o interface in the absence of surfactants under mild shear stress through membrane emulsification. The lipases showed a very high enantioselectivity (100%) at high conversion (up to 90%) in the hydrolysis of *S*-naproxen methyl ester.

4. Catalysis in Pickering Emulsions Stabilized by Amphiphilic Nanoparticles (PAC)

The catalytic systems presented in section 3 are outstanding, but not ideal. Surfactant-stabilized systems allow the increase of the interfacial area between hydrophilic and hydrophobic reagents at the nano- and microscales. However, they require the use of synthetic amphiphiles (mostly petrosourced) and product and catalyst recovery is usually difficult. In the case of MEIC, product and catalyst recovery can be overcome by resorting to multiphase μem systems, especially those of the Winsor I (i.e., a μem phase in equilibrium with an oil phase) and the Winsor III (i.e., a μem phase in equilibrium both with aqueous and oil phases) type. However, single-phase μems are not general and additives must be often used to extend their applications (e.g., cyclodextrins, co-surfactants), while multiphase μems require the addition of salts or the design of well-balanced surfactants.

Pickering emulsions combined with homogeneous catalysts (i.e., PAC) show a potential to overcome these drawbacks. Indeed, nanocrystallites, colloidosomes, polymersomes, and microgels are able to stabilize emulsions in the presence of water and oil, thus providing triphasic L/S/L systems as reaction media. The reactions proceed at competitive rates with facile phase separation by filtration, centrifugation, or heating the emulsion to the volume-phase transition temperature.

4.1. Cyclodextrins as Pickering Emulsifiers

In addition to IPTC applications, CDs can be used as emulsifiers instead of standard surfactants to perform catalytic reactions.[48] Indeed, the presence of oil phases (e.g., soybean oil, *n*-alkanes, *n*-alkanols) results in the formation of insoluble oil/CD inclusion complexes (Figure 8).[49] These solids, which are partially wettable by both water and oil, adsorb at the w/o interface to generate Pickering emulsions, offering a platform for catalysis.[49b] In 2013, Nardello-Rataj and co-workers published some prospective catalytic applications of such emulsions for the oxidation of alkenes, alcohols, and organosulfur compounds.[50] In combination with the water-soluble catalyst $Na_3[PW_{12}O_{40}]$ and H_2O_2 as an oxidant, the emulsions behaved as a highly efficient reaction medium. For example, the conversion of cyclooctene into the corresponding epoxide was 49-fold higher than that observed in the absence of emulsifier because of a promoted interfacial contact between the alkene and the catalyst.

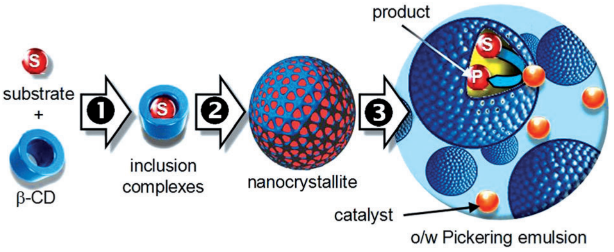


Figure 8. Principle of CD/substrate combination to perform interfacial catalysis in emulsion: 1) formation of inclusion complexes, 2) formation of nanocrystallites, 3) formation of an o/w Pickering emulsion based on nanocrystallites.

Also in 2013, Potier et al. published the rhodium-catalyzed hydroformylation of higher alkenes in Pickering emulsions based on a mixture of native α-CD and high-molecular-weight polyethylene glycol (PEG).[51] A hydrogel constituted of nanocrystallites was formed and served as physical crosslinks alongside PEG chains not included within the CD cavities. These α-CD/PEG nanocrystallites were used to stabilize o/w Pickering emulsions and increase the contact between the organic substrate and the water-soluble catalyst (Figure 9). The catalytic performance was drastically enhanced in comparison to neat biphasic conditions or in the sole presence α-CD or PEG. For example, the conversion of 1-decene was 16-fold higher than that observed in neat water and 4-fold higher than that measured using PEG as the sole additive.

4.2. Enzymes Combined with Pickering Particles

A series of recent publications have appeared that report the encapsulation of enzymes in Pickering emulsions as a means to improve their catalytic activity (Figure 10). In such systems, the enzyme behaves as a homogeneous catalyst inside the emulsion droplets stabilized by nanoparticles. In 2011, Wang and co-workers described the encapsulation of

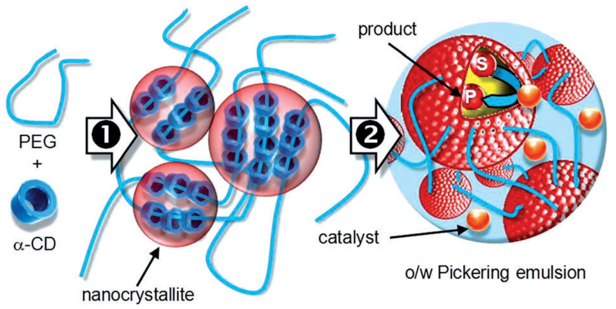


Figure 9. Principle of CD/PEG combination to perform interfacial catalysis in emulsion: 1) formation of a supramolecular hydrogel in aqueous solution with local arrangement in nanocrystallites, 2) formation of an o/w Pickering emulsion based on nanocrystallites.

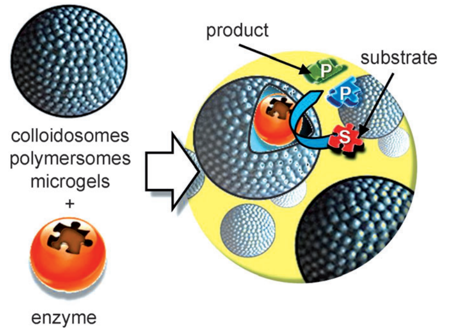


Figure 10. Principle of Pickering emulsions to perform interfacial biocatalysis in the presence of colloidosomes, polymersomes, or microgels.

enzymes gelled inside colloidosomes generated by hydrophobic silica nanoparticles.[52] A further evolution of such a concept allowed the generation of supramolecular gels in a variety of organic solvents using a crown-ether-appended, chiral supergelator based on a bis(urea) motif.[53] The gels could trap enzymes and release them on demand by chemical stimuli.

Likewise, van Hest and co-workers reported in 2012 the genesis of polymersomes (i.e., artificial vesicles)[54] stabilized by Pickering emulsions with the potential for single and cascade reactions.[55] In such systems, the enzyme can be loaded either in the water phase or in the polymersome lumen of the Pickering emulsion to enhance the catalytic performance and recyclability. Another recent example of polymersomes was published in 2013 by Richtering and co-workers who used emulsions stabilized by stimuli-responsive microgels to perform enzyme catalysis.[56] After the reaction, the Pickering emulsion could be broken up by a temperature variation to separate the reaction product and recycle the enzyme and the microgel.

5. Catalysis in Pickering Emulsions Stabilized by Catalytic Amphiphilic Nanoparticles (PIC)

As pointed out above, PAC relies on the use of nanoparticles for stabilizing Pickering emulsions together with a homogeneous catalyst, but with no intrinsic catalytic properties ascribed to the particles. PIC emerges as a logical evolution of such a concept, encompassing particles behaving concomitantly as emulsifiers and interfacial catalysts. Unlike surfactant-combined catalysis (MIC, MEIC, and SIC systems), such a concept is expected to promote the catalyst recyclability and reuse.

Examples of catalytic amphiphilic particles for performing biphasic reactions have been reported. However, in most cases, no clear location of the particles in the reaction system is provided, thus making the identification of a possible PIC effect difficult.[57] The first example of a PIC system establishing a neat correlation between the catalytic performance and emulsification in biphasic systems was published by Resasco and co-workers in 2010.[26b] In this study, the authors described the preparation of nanohybrids combining single-walled carbon nanotubes (SWCNTs) and silica-supported palladium nanoparticles, which efficiently catalyzed biofuel-upgrade reactions by generating w/o emulsions.

In the following lines, we provide a systematic compilation of PIC systems and their main prospects for biphasic reactions. In general terms, amphiphilic catalysts for PIC reactions can be broadly classified into three families: 1) composite materials bearing both hydrophilic and hydrophobic moieties for acid-catalyzed reactions, 2) nanohybrids for oxidation, reduction, and hydrogenolysis reactions, and 3) heterogenized homogeneous catalysts and enzymes for acid and oxidation catalysis.

5.1. Amphiphilic Acid/Base Catalysts

Examples of acid–base amphiphilic catalysts operating by the PIC principle are scarce. In a pioneering study, Resasco and co-workers published a catalytic system based on HY zeolites decorated with hydrophobic octadecyl chains at the external surface (chains grafted by silylation; Figure 11).[58] The modified zeolites stabilized the zeolite structure and protected the Brønsted and Lewis acidic sites against deactivation. This resulted in an outstanding enhancement of the catalytic activity, regenerability, and reusability in the alkylation of *m*-cresol with 2-propanol in a water/decalin Pickering emulsion. Indeed, the modified zeolite afforded a *m*-cresol conversion of 35 % at 200 °C after 5 hours of reaction, whereas the parent zeolite only achieved 10 % conversion and was completely deactivated after the first catalytic cycle.

Recently, two examples of amphiphilic silica particles incorporating propanesulfonic acid groups and octyl or octadecyl chains for acid-catalyzed condensation reactions have been reported. In a first study, the enhanced acetalyzation of fatty aldehydes with ethylene glycol in an alcohol/aldehyde Pickering emulsion was demonstrated using amphiphilic silica nanoparticles prepared by co-precipitation and bearing a high density of alkyl chains and silanol groups (>20 alkyl groups per nm^2 and >33 SiOH per nm^2 for octadecyl-functionalized silica; Figure 12).[59] Interestingly, the reaction progressed faster in the presence of the amphiphilic silica, attaining chemical equilibrium after 1 hour at 60 °C. In contrast, the same reaction performed in the presence of *p*-

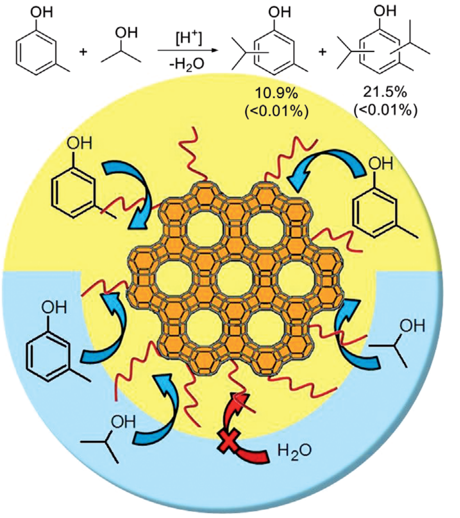


Figure 11. Principle of a PIC system based on zeolites functionalized with hydrophobic alkyl chains to perform the acid-catalyzed *m*-cresol alkylation with 2-propanol in w/o emulsion for fuel upgrading. The numbers below the reaction products indicate the yield after two consecutive runs (top values) and in a monophasic system (lower values in parentheses). Reaction conditions: 200 °C, 3 h, 2-propanol/*m*-cresol ratio = 3, concentration = 2 M, 500 mg catalyst, 700 psig He.

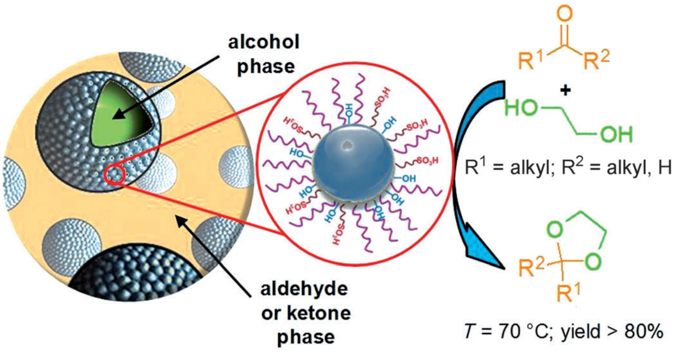


Figure 12. Principle of a PIC system based on amphiphilic silica nanoparticles incorporating alkane sulfonic catalytic sites, alkyl chains, and surface silanol groups to perform the acid-catalyzed acetalization of fatty aldehydes and ketones with ethylene glycol in emulsion.

toluenesulfonic acid (PTSA) at a concentration providing the same number of acid equivalents only attained equilibrium after 24 hours. The promoted activity was ascribed to the formation of stable ethylene glycol/aldehyde emulsions favoring the contact between the reagents.

In a more recent study, amphiphilic silica nanoparticles have been used to perform the solvent-free etherification of glycerol with dodecanol.[60] In this case, Aerosil-type silica nanoparticles grafted with propanesulfonic acid sites and propyl chains as hydrophobic moieties stabilized glycerol/dodecanol Pickering emulsions, even at high temperature. The modified silica nanoparticles were able to activate the interfacial reaction of both reactants at 150 °C and showed a 30-fold increase of the catalytic activity compared to that of either PTSA or propyl-grafted silica combined with PTSA.

In 2011, Guo and co-workers reported the preparation of mesoporous sulfated zirconia materials functionalized with ethyl and phenylsilyl moieties with variable S/Si and Zr/Si molar ratios, affording the genesis of amphiphilic nanoparticles.[61] The materials were prepared by a one-step co-condensation technique combined with a hydrothermal treatment using the P123 surfactant as a structure-directing agent. The materials offered a prominent catalytic activity and stability in the transesterification of both pure triglyceride (tripalmitin) and low-cost virgin plant oil (*Eruca sativa* Gars oil) with methanol at 65 °C and ambient pressure. Noticeably, the materials displayed an enhanced catalytic activity with respect to alkyl-free sulfated zirconia, which was attributed to the inherent Brønsted acidity of the particles, as well as the simultaneous formation of Pickering emulsions.

In addition to amphiphilic Brønsted acidic catalysts, Khalafi-Nezhad et al. recently prepared a surfactant-combined Lewis acidic catalyst by immobilization of nano-TiO_2 on dodecylsulfated silica.[62] The catalyst was successfully used in the synthesis of coumarin derivatives by Pechmann condensation in water, affording moderate to high yields. The authors pointed out the formation of water droplets stabilized by the amphiphilic catalyst as the key element promoting the interfacial contact between the reagents (i.e., phenol and β-ketoester or lactone).

In 2010, Nawaratna et al. reported the first and sole example to date of rationally designed amphiphilic nanoparticles for base-catalyzed reactions.[63] Inspired by a former study on amphiphilic titanium alkoxide oligomers (see Ref. [34] and section 3.1), the authors prepared titanium-isopropoxide-based inorganic dendritic polymers with variable degrees of polymerization (Figure 13). The polymers showed a high catalytic performance in the transesterification of soybean oil, achieving a 42 % yield of the propyl esters at 200 °C after 3 hours of reaction with 1 wt. % of the monomeric form of the catalyst.

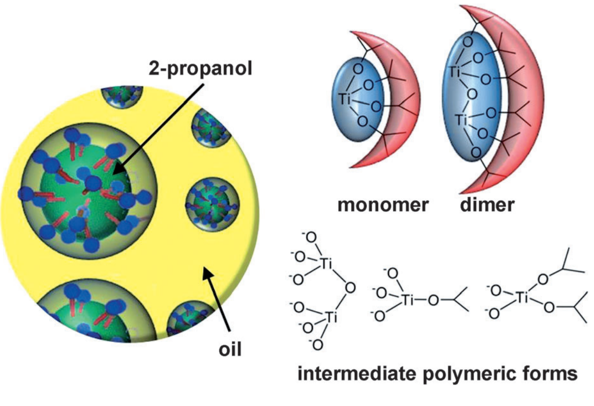


Figure 13. Principle of a PIC system based on monomeric titanium isopropoxide to perform the base-catalyzed transesterification of soybean oil with 2-propanol in alcohol/oil emulsion.

5.2. Amphiphilic Oxidation/Epoxidation Catalysts

Carbonaceous materials can easily become amphiphilic after treatment with a mixture of H_2SO_4 and HNO_3, affording the genesis of Pickering emulsions. Nanohybrid catalysts based on ruthenium nanoparticles supported over CNTs and

CNTs–TiO_2 composites were used to perform the oxidation of alcohols under air or oxygen.[64] The partial oxidation of benzyl alcohol was enhanced and quickened in the presence of water because of the formation of emulsion droplets. Moreover, this Ru/CNT catalyst could be easily recovered by sedimentation and reused. Au, Ag, Pd, or Fe_3O_4 were also supported over porous hollow carbonaceous spheres (PHCSs) to perform phase-transfer reactions in biphasic systems.[65] The particles could form stable o/w Pickering emulsions displaying an eye-catching reversible pH-dependent phase-transfer behavior.

In line with the aforementioned studies, Moura and co-workers recently developed magnetic nanohybrids by growing CNTs and nanofibers (CNFs) on Fe–Mn supported over alumina and on red mud using a chemical vapor deposition (CVD) technique.[66] The catalysts were subsequently used in the biphasic oxidation of Sudan IV, thiophene, dibenzothiophene (DBT), and quinolone using H_2O_2 as an oxidant (Fenton reaction) in an o/w emulsion, reaching almost full degradation. After the reaction, the emulsion could be easily broken up by a magnetic process, affording a facile separation of the decontaminated water phase and the catalyst. In a separate study, Oliveira et al. developed an amphiphilic niobium oxyhydroxide catalyst with anchored CTA chains for the oxidative desulfurization of DBT with H_2O_2 in an acetonitrile/*n*-hexane emulsion.[67] The authors proposed a catalytic mechanism driven by a single-oxygen transfer from the surface of the substrate with no radical formation. Finally, Zhang and co-workers developed a composite catalyst based on $[BMIM]_3[PW_{12}O_{40}]$ (BMIM = 1-butyl-3-methylimidazolium) supported over silica for oxidative desulfurization with H_2O_2.[68] A silica-supported catalyst with 20 wt.% $[BMIM]_3[PW_{12}O_{40}]$ exhibited the highest activity resulting from the formation of Pickering emulsions, achieving almost full DBT oxidation at 50 °C for 100 minutes. The catalyst could be conveniently recycled by filtration and reused for at least seven times with no significant reduction in activity.

Other examples of nanohybrid materials have been reported for the photocatalytic degradation of organic pollutants. In 2013, Mao and co-workers showed that Ag_3PO_4 supported over multiwalled carbon nanotubes (MWCNTs) could stabilize w/o Pickering emulsions and enhance the photocatalytic degradation of methylene blue and the production of O_2 from water splitting (Figure 14).[69] Additional examples cover surfactant-combined photocatalysts for the degradation of organic pollutants in w/o emulsions. Examples of such systems include the TiO_2–salicylic acid nanoparticles developed by Chevalier and co-workers,[70a] and the layered niobate $K_4[Nb_6O_{17}]$ intercalated with alkylammonium cations, reported by Nakato and co-workers, with an adjustable hydrophilic/hydrophobic balance.[70b] Finally, Zhang and co-workers prepared ZnO particles modified with titanium isopropoxide tris(di(2-ethylhexyl)phosphate) as coupling reagent, affording almost complete nitrobenzene removal after 80 minutes, for ZnO particles with 3–5 wt.% of the titanate reagent, by stabilization of nitrobenzene/water Pickering emulsions.[71]

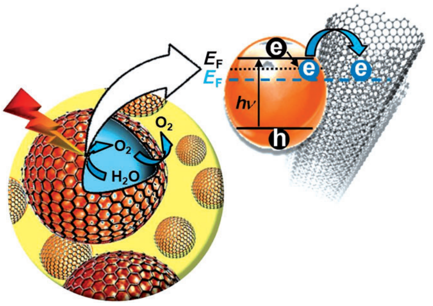


Figure 14. Schematic representation of a Pickering-emulsion-based photocatalytic system formed by the self-assembly of Ag_3PO_4/MWCNT nanohybrids at the w/o interface to produce O_2 from water splitting.

In addition to (photo)oxidation systems, Nardello-Rataj and co-workers developed specific catalytic systems for epoxidation reactions using H_2O_2 as an oxidant.[72] The authors prepared water/aromatic solvent Pickering emulsions stabilized by catalytic POM nanoparticles incorporating decyl-, dodecyl-, and tetradecyltrimethylammonium chains (Figure 15). Quantitative cyclooctene, cyclohexene, and limonene epoxidation could be achieved at 65 °C in water/toluene emulsions using POM nanoparticles incorporating dodecyltrimethylammonium chains with easy product and catalyst separation. Likewise, Leng and co-workers developed an amphiphilic POM-paired ionic copolymer by anion exchange of an ionic liquid copolymer with $H_3[PW_4O_{16}]$.[73] The catalyst offered great activity and versatility in the epoxidation of olefins with H_2O_2 by stabilizing w/o Pickering emulsions. After the reaction, the catalyst could be conveniently recovered and reused without any obvious structural change. In 2010, Wu and co-workers prepared a new type of catalyst based on surfactant-encapsulated POM by co-condensation (sol–gel) of hydroxy-terminated surfactant-encapsulated POM complexes with tetraethyl orthosilicate.[74] The hybrid catalysts possessed a defined hydrophobic nanoenvironment surrounding the inorganic clusters, thus affording the formation of stable Pickering emulsions. The catalysts were efficient in the selective oxidation/epoxidation of alkenes, alcohols, and sulfides, and could be easily recovered by simple filtration, with the catalytic activity maintained for at least five cycles.

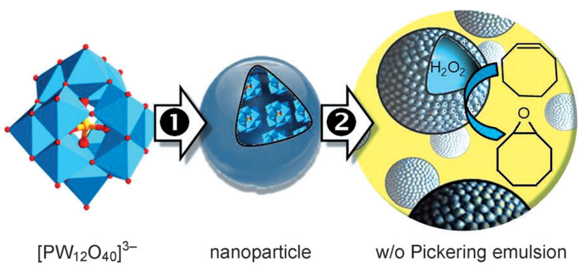


Figure 15. Principle of cyclooctene epoxidation in a w/o emulsion stabilized by catalytic nanoparticles formed by a POM and alkylammonium cations. 1) Formation of nanoparticles; 2) stabilization of Pickering emulsions and interfacial catalysis.

Finally, in addition to POM systems, Zheng et al. reported very recently magnetic amphiphilic polystyrene nanospheres with covalently tethered 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO).[75] These catalysts showed a much higher activity than their soluble counterparts for the Montanari oxidation of a series of aromatic and aliphatic alcohols in w/o Pickering emulsions using NaClO as an oxidant (by a factor of 3). Furthermore, the catalysts could be efficiently recycled by magnetic decantation and reused for at least 10 times without significant loss of activity or degradation of magnetic susceptibility.

5.3. Amphihilic Reduction/Hydrogenation Catalysts

The first example of a PIC system affording catalytic reduction was reported by Zhou and co-workers in 2011.[65] These authors showed that gold supported over PHCSs behaved as an efficient catalyst in the reduction of *p*-nitroanisole with sodium sulfide and $NaBH_4$. The particles could be recycled and reused after reaction with no catalyst deactivation.

Recently, two additional examples of PIC systems, based on gold and silver nanoparticles, respectively, supported over graphene oxide, have been published.[76] Both systems were very active in the reduction of 4-nitrophenol with $NaBH_4$ by stabilizing o/w Pickering emulsions, even if the former showed a decrease in activity after recycling. Multiple w/o/w emulsions were generated at low graphene oxide concentration, low pH, high o/w ratio, and high salt concentration, paving the way to possible cascade reactions.

In 2013 Yang and co-workers published an outstanding study on the rational design of palladium nanoparticles supported over amphiphilic silica microspheres for the hydrogenation of styrene with dissolved H_2 in an ethyl acetate/water emulsion.[77] The amphiphilic properties of the silica microspheres could be tuned by changing the relative density of alkyl (C_8) and aminoalkyl groups, the latter being pH sensitive. Indeed, the reaction product could be easily separated and the catalyst recycled by inversing the Pickering emulsion after reaction (i.e. o/w) without the need of desorption. By such an approach, the catalyst could be recycled for more than 36 successive cycles with negligible loss in activity.

In a subsequent study, the same team has recently shown that the formulation of densely packed Pickering emulsions can be used as a tool for performing organic/aqueous reactions without stirring.[78] Using nitrotoluene reduction with $NaBH_4$ in water as model reaction system, the authors showed a comparable reaction efficiency to conventional stirrer-driven biphasic catalysis.

5.4. Amphiphilic Hydrogenolysis Catalysts

Palladium nanoparticles supported over carbonaceous supports [CNT/silica nanohybrids, mesoporous N-doped carbon, carbon microspheres (CMs)] have been described for the hydrodeoxygenation (HDO) of vanillin in the presence of w/o emulsions.[26b,79] The hydrophilic properties of Pd/CMs could be promoted by hydrothermal post-treatment, resulting in a higher catalytic activity for vanillin HDO with a higher selectivity to *p*-cresol. The catalysts could be easily separated from the reaction medium and reused.

Vanillin HDO as a biofuel-upgrade model reaction was also performed with a water/decalin Pickering emulsion using Ru/CNT as the Pickering catalyst, which showed excellent activity and selectivity under mild reaction conditions.[80] Depending on the reaction temperature, the reaction could be oriented to the formation of either vanillyl alcohol (50 °C, 98 % yield) or *p*-cresol (100 °C, 96 % yield). The nanoparticles distributed preferentially at the surface of the emulsion droplets, as inferred by using fluorescently labeled probes.

5.5. Amphiphilic Catalysts for Cascade Reactions

The most innovative and attractive development of the PIC concept involves catalytic systems affording cascade reactions. Resasco and co-workers published two examples of SWCNT/silica and SWCNT/MgO nanohybrids which catalyzed the tandem aldolization reaction of 5-methylfurfural with acetone followed by hydrogenation of the aldol product, driven by a partial phase transfer (i.e., phase-selective catalysis; Figure 16).[26b,81] In a separate study, the same team compared the performance of palladium and copper supported on different types of CNTs fused to silica and alumina, such as onion-like carbon, SWCNT, and MWCNT.[82] The catalysts were tested on three model reactions: 1) hydrogenation of phenanthrene, 2) competitive hydrogenation of glutaraldehyde and benzaldehyde, and 3) oxidation of tetralin with air. For the first reaction, the authors correlated the catalytic performance of the nanohybrids not only to the formation of a Pickering emulsion but also to its nature. For the second reaction, the authors reported a high selectivity in the hydrogenation of the aldehydes in one of the two phases by an anisotropic distribution of the palladium clusters sitting at the L/L interface near the active phase. Finally, for the third reaction, copper supported on alumina-based nanohybrids reflected an improved catalytic performance in the emulsion system compared to that of the monophasic system for the partial oxidation of tetralin.

More recently, Resasco and co-workers published two new applications of nanohybrid catalysts for enhanced oil recovery (EOR) and Fischer–Tropsch synthesis of fuels.[83] On the one hand, in the former study,[83a] the authors reported a comparable performance to that currently obtained by the injection of benchmark surfactant and polymer solutions. Interestingly, the supported metal could act as both an oxidative and a reductive catalyst while simultaneously decreasing the interfacial tension and increasing the viscosity of the sweeping phase. On the other hand, in the latter development,[83b] the authors used ruthenium supported over MWCNT/MgO–Al_2O_3 as a catalyst to perform the Fischer–Tropsch synthesis of fuels at the w/o interface, leading to a three-layered liquid structure (oil/emulsion/water). The hydrocarbons migrated to the top phase, while short alcohols remained at the bottom phase, facilitating the separation of the reaction products. High CO conversion rates were also observed.

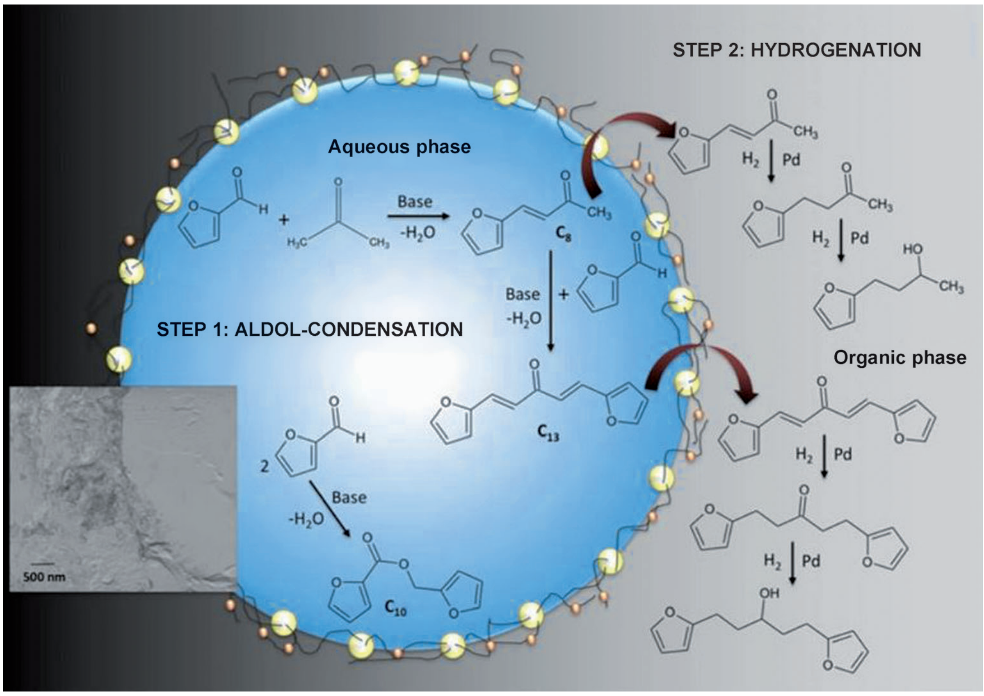


Figure 16. Schematic illustration of the aldol condensation and sequential hydrogenation at the w/o interface in emulsions stabilized by MWCNT/SiO$_2$ and MWCNT/MgO nanohybrids. Reprinted with permission from Reference [81]. Copyright (2012) Springer Science.

5.6. Amphiphilic Nanoparticles with Immobilized Enzymes

As pointed out in section 4.2, the use of nanoparticles to promote Pickering emulsions as a tool to trap enzymes within emulsion droplets (i.e., colloidosomes and polymersomes) can boost, to an important extent, the enzymatic activity. However, in such systems, the nanoparticles and enzymes have to be separated and recycled, leading to cumbersome processes.

As a solution to this shortcoming, Li and co-workers recently demonstrated the encapsulation of lipases into the nanocages of FDU-12 mesoporous silica (FDU = Fudan University Silica) without significant enzyme leaching after hydrophobic modification of the silica by silylation (Figure 17).[84] The hybrid particles could generate stable w/o Pickering emulsions with enhanced catalytic properties in both triacetin hydrolysis and the kinetic resolution of (*R*,*S*)-1-phenylethanol. The particles could be easily recycled and reused several times. Very recently, Gao and co-workers applied a similar strategy by encapsulating a lipase within periodic mesoporous silica to catalyze the esterification of fatty acids with alcohols and the transesterification of triglycerides.[85] The system could generate stable Pickering emulsions, resulting in an enhanced catalytic activity, stability, and reusability compared to the native lipase.

As an alternative approach, Hou et al. succeeded in the covalent attachment of lipases to macroporous polystyrene, modified with polyamidoamine dendrimers (PS-PAMAM dendrimers), as an enzyme carrier (Figure 18).[86] The enzyme-immobilized particles behaved as an active biocatalyst in the hydrolysis of an olive oil emulsion, keeping more than 50% of the initial activity before immobilization and only showing slight deactivation after 10 rounds of recycling.

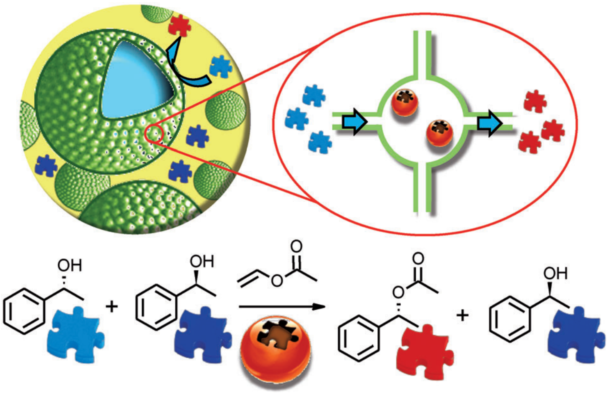


Figure 17. Lipase encapsulated in silica nanocages to perform the kinetic resolution of *(R,S)*-1-phenylethanol (or the hydrolysis of triacetin; not shown in the Figure).

6. Conclusions

Throughout this Minireview, we have presented a systematic compilation of recent examples of PIC systems affording solvent-free biphasic reactions at the liquid–liquid interface for the synthesis of fine chemicals and the conception of depollution processes, which are in most cases out of reach of current technologies. We have shown that a smart design of the catalysts presenting tunable amphiphilic properties can promote the catalytic activity by the formation of Pickering emulsions, which improves mass-transfer of the reagents to the active sites. Following this concept, domino/cascade reactions might be driven by preferential phase-transfer separation, offering a new platform for the one-pot synthesis

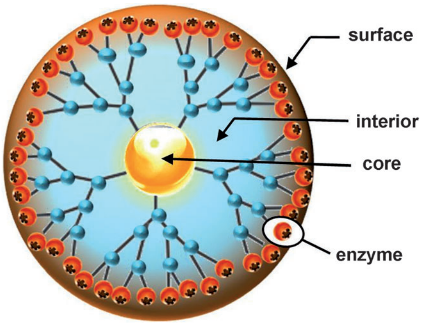


Figure 18. Schematic illustration of immobilized enzymes (lipases) in PS-PAMAM.

of complex organic molecules with no need of protection of functional groups.

The examples stated above demonstrate the value of PIC systems for biphasic reactions as well as their potential application to processes of industrial interest. However, it appears that the mechanisms driving the increased activity and the control of various reaction parameters are still poorly understood, opening an avenue for future improvements. To this end, the development of devoted in silico tools, which are nonexistent at present, could help and assist the design of Pickering catalysts à la carte for industrially relevant biphasic reactions.

Last but not least, the development of well-adapted tools for catalyst recovery or recycling still constitutes an unsolved challenge. Possible strategies for boosting catalyst recovery include a careful control of adsorption energy by tuning the particle size and contact angle, as well as the formulation of smart systems allowing emulsion inversion on demand with external controllable stimuli using thermo-, pH-, light-, or electromagnetic-responsive catalytic nanoparticles (see for instance Ref. [87]).

Glossary

CD:	Cyclodextrin
CM:	Carbon microsphere
CTA:	Cetyltrimethylammonium
DBSA:	Dodecylbenzene sulfonic acid
DBT:	Dibenzothiophene
DS:	Dodecylsulfate
EC:	Emulsion catalysis
EO:	Ethylene oxide
IPTC:	Inverse phase-transfer catalysis
MAC:	Micellar-assisted catalysis
MC:	Micellar catalysis
MEAC:	Microemulsion-assisted catalysis
MEC:	Microemulsion catalysis
MEIPTC:	Microemulsion inverse phase-transfer catalysis
MEIC:	Microemulsion interfacial catalysis
MIC:	Micellar interfacial catalysis
MIPTC:	Micellar inverse phase-transfer catalysis
MWCNT:	Multiwalled carbon nanotube
Q:	Quaternary ammonium cations
PAC:	Pickering-assisted catalysis
PAMAM:	Polyamidoamine
PBC:	Phase-boundary catalysis
PEC:	Pickering emulsion catalysis
PEG:	Polyethylene glycol
PHCS:	Porous hollow carbonaceous spheres
PIC:	Pickering interfacial catalysis
POM:	Polyoxometalate
PS:	Polystyrene
PTC:	Phase-transfer catalysis
PTSA:	*p*-Toluenesulfonic acid
SAC:	Surfactant-assisted catalysis
SEC:	Surfactant emulsion catalysis
SIC:	Surfactant interfacial catalysis
SWCNT:	Single-walled carbon nanotube

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[1] "Catalytic conversion of biosourced raw materials: homogeneous catalysis": C. Fischmeister, C. Bruneau, K. De Oliveira Vigier, F. Jérôme in *Biorefinery: From Biomass to Chemicals and Fuels* (Eds.: M. Aresta, A. Dibenedetto, F. Dumeignil), De Gruyter, Berlin, **2012**, p. 231.

[2] M. Lombardo, A. Quintavalla, M. Chiarucci, C. Trombini, *Synlett* **2010**, 1746–1765.

[3] *Market Study: Solvents*, 3rd ed., Ceresana Research, available brochure at http://www.ceresana.com/en/market-studies/chemicals/solvents/solvents-market-share-capacity-demand-supply-forecast-innovation-application-growth-production-size-industry.html. This link will only work till the next edition of this study will have appeared. A more general link is: http://www.ceresana.com/en.

[4] Y. Gu, F. Jérôme, *Chem. Soc. Rev.* **2013**, *42*, 9550–9570.

[5] P. Trambouze, J. P. Euzen, *Chemical Reactors: From Design to Operation*, EditionsTechnip, Paris, **2004**.

[6] K. S. Elvira, X. C. Solvas, R. C. R. Wootton, A. J. deMello, *Nat. Chem.* **2013**, *5*, 905–915.

[7] a) T. Ooi, K. Maruoka, *Angew. Chem. Int. Ed.* **2007**, *46*, 4222–4266; *Angew. Chem.* **2007**, *119*, 4300–4345; b) "The Basic Principle of Phase-Transfer Catalysis and Some Mechanistic Aspects": T. Hashimoto, K. Maruoka in *Asymmetric Phase Transfer Catalysis*, Chap. 1 (Ed.: K. Maruoka), Wiley-VCH, Weinheim, **2008**.

[8] "Rhodium-catalyzed hydroformylation promoted by modified cyclodextrins: current scope and future developments": F. Harpiot, L. Leclercq, N. Azaroual, S. Fourmentin, S. Tilloy, E. Monflier in *Advances in Organic Synthesis, Vol. 4* (Ed.: Atta-ur-Rehman), Bentham Science, Sharjah, **2013**, pp. 37.

[9] a) S. Shimizu, N. Shimada, Y. Sasaki, *Green Chem.* **2006**, *8*, 608–614; b) Y. L. Liu, L. Liu, Y. L. Wang, Y. C. Han, D. Wang, Y. J. Chen, *Green Chem.* **2008**, *10*, 635–640.

[10] H. Nur, S. Ikeda, B. Ohtani, *Chem. Commun.* **2000**, 2235–2236; H. Nur, S. Ikeda, B. Ohtani, *J. Catal.* **2001**, *204*, 402–408; H. Nur, S. Ikeda, B. Ohtani, *J. Braz. Chem. Soc.* **2004**, *15*, 719–724.

[11] S. Mukhopadhyay, G. Rothenberg, N. Qafisheh, Y. Sasson, *Tetrahedron Lett.* **2001**, *42*, 6117–6119.

[12] L. D. Pachón, C. J. Elsevier, G. Rothenberg, *Adv. Synth. Catal.* **2006**, *348*, 1705–1710.

[13] B. Boyer, A. Hambardzoumian, J.-P. Roque, N. Beylerian, *Tetrahedron* **2000**, *56*, 303–307.

[14] T. Dwars, E. Paetzold, G. Oehme, *Angew. Chem. Int. Ed.* **2005**, *44*, 7174 – 7193; *Angew. Chem.* **2005**, *117*, 7338 – 7364.

[15] a) S. Otto, J. B. F. N. Engberts, J. C. T. Kwak, *J. Am. Chem. Soc.* **1998**, *120*, 9517 – 9525; b) V. Touchard, C. Graillat, C. Boisson, F. D'Agosto, R. Spitz, *Macromolecules* **2004**, *37*, 3136 – 3142; c) V. V. Vasilevskaya, A. A. Aerov, A. R. Khokhlov, *Colloid Polym. Sci.* **2006**, *284*, 459 – 467; d) E. M. Aschenbrenner, C. K. Weiss, K. Landfester, *Chem. Eur. J.* **2009**, *15*, 2434 – 2444; e) J. Zhao, H. Guan, W. Shi, M. Cheng, X. Wang, S. Li, *Catal. Commun.* **2012**, *20*, 103 – 106; f) H. R. Safaei, M. Shekouhy, S. Khademi, V. Rahmanian, M. Safaei, *J. Ind. Eng. Chem.* **2014**, *20*, 3019 – 3024.

[16] M. Häger, K. Holmberg, *Chem. Eur. J.* **2004**, *10*, 5460 – 5466.

[17] a) L. Jing, X. J. Li, Y. C. Han, Y. Chu, *Colloids Surf. A* **2008**, *326*, 37 – 41; b) K. Song, Y. Chu, L. Dong, J. Song, D. Wang, *J. Mol. Catal. A* **2008**, *282*, 144 – 148.

[18] a) V. Nardello-Rataj, L. Caron, C. Borde, J.-M. Aubry, *J. Am. Chem. Soc.* **2008**, *130*, 14914 – 14915; b) M. Fressancourt-Collinet, B. Hong, L. Leclercq, P. L. Alsters, J.-M. Aubry, V. Nardello-Rataj, *Adv. Synth. Catal.* **2013**, *355*, 409 – 420.

[19] M. Shiri, M. A. Zolfigol, *Tetrahedron* **2009**, *65*, 587 – 598.

[20] Lewis acids: K. Manabe, S. Kobayashi, *Synlett* **1999**, 547 – 548; S. Kobayashi, Y. Mori, S. Nagayama, K. Manabe, *Green Chem.* **1999**, *1*, 175 – 177; K. Manabe, Y. Mori, T. Wakabayashi, S. Nagayama, S. Kobayashi, *J. Am. Chem. Soc.* **2000**, *122*, 7202 – 7207; K. Manabe, S. Kobayashi, *Chem. Commun.* **2000**, 669 – 670; Y. Mori, K. Kakumoto, K. Manabe, S. Kobayashi, *Tetrahedron Lett.* **2000**, *41*, 3107 – 3111; K. Manabe, N. Aoyama, S. Kobayashi, *Adv. Synth. Catal.* **2001**, *343*, 174 – 176; S. Azoulay, K. Manabe, S. Kobayashi, *Org. Lett.* **2005**, *7*, 4593 – 4595; Brønsted acids: K. Manabe, Y. Mori, S. Kobayashi, *Synlett* **1999**, 1401 – 1402; K. Manabe, S. Kobayashi, *Org. Lett.* **1999**, *1*, 1965 – 1967; K. Manabe, Y. Mori, S. Kobayashi, *Tetrahedron* **2001**, *57*, 2537 – 2544; K. Manabe, S. Iimura, X.-M. Sun, S. Kobayashi, *J. Am. Chem. Soc.* **2002**, *124*, 11971 – 11978; S. Shirakawa, S. Kobayashi, *Org. Lett.* **2007**, *9*, 311 – 314; K. Manabe, X.-M. Sun, S. Kobayashi, *J. Am. Chem. Soc.* **2001**, *123*, 10101 – 10111; K. Manabe, S. Kobayashi, *Org. Lett.* **2006**, *6*, 311 – 314.

[21] a) Y. Hayashi, S. Aratake, T. Okano, J. Takahashi, T. Sumiya, M. Shoji, *Angew. Chem. Int. Ed.* **2006**, *45*, 5527 – 5529; *Angew. Chem.* **2006**, *118*, 5653 – 5655; b) S. Luo, X. Mi, S. Liu, H. Xua, J. P. Cheng, *Chem. Commun.* **2006**, 3687 – 3689; c) L. Zhong, Q. Gao, J. Gao, J. Xiao, C. Li, *J. Catal.* **2007**, *250*, 360 – 364; d) M. Lombardo, S. Easwar, A. De Marco, F. Pasia, C. Tromboni, *Org. Biomol. Chem.* **2008**, *6*, 4224 – 4229; e) B. Zhang, Z. Jiang, X. Zhou, S. Lu, J. Li, Y. Liu, C. Li, *Angew. Chem. Int. Ed.* **2012**, *51*, 13159 – 13162; *Angew. Chem.* **2012**, *124*, 13336 – 13339.

[22] a) S. Narayan, J. Muldoon, M. G. Finn, V. V. Fokin, H. C. Kolb, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2005**, *44*, 3275 – 3279; *Angew. Chem.* **2005**, *117*, 3339 – 3343; b) Y. Jung, R. A. Marcus, *J. Am. Chem. Soc.* **2007**, *129*, 5492 – 5502.

[23] P. Norcott, C. Spielman, C. S. P. McErlean, *Green Chem.* **2012**, *14*, 605 – 609.

[24] a) B. P. Binks, *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 21 – 41; b) R. Aveyard, B. P. Binks, J. H. Clint, *Adv. Colloid Interface Sci.* **2003**, *100 – 102*, 503 – 546; c) F. Leal-Calderon, V. Schmitt, *Curr. Opin. Colloid Interface Sci.* **2008**, *13*, 217 – 227.

[25] S. Sacanna, W. K. Kegel, A. P. Philipse, *Phys. Rev. Lett.* **2007**, *98*, 158301.

[26] a) D. J. Cole-Hamilton, *Science* **2010**, *327*, 41 – 42; b) S. Crossley, J. Faria, M. Shen, D. E. Resasco, *Science* **2010**, *327*, 68 – 72.

[27] L. Gang, L. Xinzong, W. Eli, *New J. Chem.* **2007**, *31*, 348 – 351.

[28] a) G. F. Ghesti, J. L. de Macedo, V. C. I. Parente, J. A. Dias, S. C. L. Dias, *Appl. Catal. A* **2009**, *355*, 139 – 147; b) F. C. G. de Mattos, J. A. D. de Souza, A. B. D. Cotrim, J. L. de Macedo, J. A. Dias, S. C. L. Dias, G. F. Ghesti, *Appl. Catal. A* **2012**, *423*, 1 – 6.

[29] P. Gaudin, R. Jacquot, P. Marion, Y. Pouilloux, F. Jérôme, *ChemSusChem* **2011**, *4*, 719 – 722.

[30] W. He, Y. Ma, X. Pan, J. Li, M. Wang, Y. Yang, C. Jia, X. Zhang, B. Feng, *J. Agric. Food Chem.* **2012**, *60*, 9763 – 9769.

[31] Y. Zhou, C. Jia, R. Li, X. Zhang, W. He, J. Li, B. Feng, Q. Xia, *Eur. J. Lipid Sci. Technol.* **2012**, *114*, 896 – 904.

[32] H. Li, J. Chen, L. Hua, Y. Qiao, Y. Yu, Z. Pan, H. Yang, Z. Hou, *Pure Appl. Chem.* **2012**, *84*, 541 – 551.

[33] Q. Wu, H. Wan, H. Li, H. Song, T. Chu, *Catal. Today* **2013**, *200*, 74 – 79.

[34] G. Nawaratna, R. Lacey, S. D. Fernando, *Catal. Sci. Technol.* **2012**, *2*, 364 – 372.

[35] B. S. Lane, K. Burgess, *Chem. Rev.* **2003**, *103*, 2457 – 2473.

[36] J. Gao, Y. Chen, B. Han, Z. Feng, C. Li, N. Zhou, S. Gao, Z. Xi, *J. Mol. Catal. A* **2004**, *210*, 197 – 204.

[37] C. Li, J. Gao, Z. Jiang, S. Wang, H. Lu, Y. Yang, F. Jing, *Top. Catal.* **2005**, *35*, 169 – 175.

[38] W. Zhu, H. Li, X. He, Q. Zhang, H. Shu, Y. Yan, *Catal. Commun.* **2008**, *9*, 551 – 555.

[39] a) C. Li, Z. Jiang, J. Gao, Y. Yang, S. Wang, F. Tian, F. Sun, X. Sun, P. Ying, C. Han, *Chem. Eur. J.* **2004**, *10*, 2277 – 2280; b) H. Lu, J. Gao, Z. Jiang, F. Jing, Y. Yang, G. Wang, C. Li, *J. Catal.* **2006**, *239*, 369 – 375; c) J. Gao, S. Wang, Z. Jiang, H. Lu, Y. Yang, F. Jing, C. Li, *J. Mol. Catal. A* **2006**, *258*, 261 – 266; d) H. Lu, J. Gao, Z. Jiang, Y. Yang, B. Song, C. Li, *Chem. Commun.* **2007**, 150 – 152; e) J. Gao, Y. Zhang, G. Jia, Z. Jiang, S. Wang, H. Lu, B. Song, C. Li, *Chem. Commun.* **2008**, 332 – 334; f) J. Ge, Y. Zhou, Y. Yang, M. Xue, *Ind. Eng. Chem. Res.* **2011**, *50*, 13686 – 13692; g) W. Zhu, G. Zhu, H. Li, Y. Chao, Y. Chang, G. Chen, C. Han, *J. Mol. Catal. A* **2011**, *347*, 8 – 14; h) J. Xu, S. Zhao, Y. Ji, Y.-F. Song, *Chem. Eur. J.* **2013**, *19*, 709 – 715; i) Y. Qiao, L. Hua, J. Chen, N. Theyssen, W. Leitner, Z. Hou, *J. Mol. Catal. A* **2013**, *380*, 43 – 48.

[40] P. Yin, J. Wang, Z. Xiao, P. Wu, Y. Wei, T. Liu, *Chem. Eur. J.* **2012**, *18*, 9174 – 9178.

[41] T. Nagano, S. Kobayashi, *Chem. Lett.* **2008**, *37*, 1042 – 1043.

[42] J. Li, Y. Zhang, D. Han, G. Jia, J. Gao, L. Zhong, C. Li, *Green Chem.* **2008**, *10*, 608 – 611.

[43] L. Leclercq, M. Lacour, S. H. Sanon, A. R. Schmitzer, *Chem. Eur. J.* **2009**, *15*, 6327 – 6331.

[44] M. Ferreira, H. Bricout, N. Azaroual, D. Landy, S. Tilloy, F. Hapiot, E. Monflier, *Adv. Synth. Catal.* **2012**, *354*, 1337 – 1346.

[45] S. Saktaweewong, P. Phinyocheep, C. Ulmer, E. Marie, A. Durand, P. Inprakhon, *J. Mol. Catal. B* **2011**, *70*, 8 – 16.

[46] S. Debnath, A. Dasgupta, R. N. Mitra, P. K. Das, *Langmuir* **2006**, *22*, 8732 – 8740.

[47] L. Giorno, E. Piacentini, R. Mazzei, E. Drioli, *J. Membr. Sci.* **2008**, *317*, 19 – 25.

[48] K. Shimada, Y. Ohe, T. Ohguni, K. Kawano, J. Ishii, T. Nakamure, *Nippon Shokuhin Kogyo Gakkaishi* **1991**, *38*, 16 – 20.

[49] a) M. Inoue, K. Hashizaki, H. Taguchi, Y. Saito, *J. Dispersion Sci. Technol.* **2010**, *31*, 1648 – 1651; b) L. Davarpanah, F. Vahabzadeh, *Starch/Staerke* **2012**, *64*, 898 – 913.

[50] L. Leclercq, R. Company, A. Mühlbauer, A. Mouret, J.-M. Aubry, V. Nardello-Rataj, *ChemSusChem* **2013**, *6*, 1533 – 1540.

[51] J. Potier, S. Menuel, M.-H. Chambrier, L. Burylo, J.-F. Blach, P. Woisel, E. Monflier, F. Hapiot, *ACS Catal.* **2013**, *3*, 1618 – 1621.

[52] C. Wu, S. Bai, M. B. Ansorge-Schumacher, D. Wang, *Adv. Mater.* **2011**, *23*, 5694 – 5699.

[53] Z. Qi, C. Wu, P. M. de Molina, H. Sun, A. Schulz, C. Griesinger, M. Gradzielski, R. Haag, M. B. Ansorge-Schumacher, C. A. Schalley, *Chem. Eur. J.* **2013**, *19*, 10150 – 10159.

[54] B. M. Discher, Y.-Y. Won, D. S. Ege, J. C.-M. Lee, F. S. Bates, D. E. Discher, D. A. Hammer, *Science* **1999**, *284*, 1143 – 1146.

[55] a) Z. Wang, M. C. M. van Oers, F. P. J. T. Rutjes, J. C. M. van Hest, *Angew. Chem. Int. Ed.* **2012**, *51*, 10746 – 10750; *Angew. Chem.* **2012**, *124*, 10904 – 10908; b) M. C. M. van Oers, F. P. J. T.

Rutjes, J. C. M. van Hest, *Curr. Opin. Biotechnol.* **2014**, *28*, 10–16.
[56] S. Wiese, A. C. Spiess, W. Richtering, *Angew. Chem. Int. Ed.* **2013**, *52*, 576–579; *Angew. Chem.* **2013**, *125*, 604–607.
[57] D. Li, J. R. Dunlap, B. Zhao, *Langmuir* **2008**, *24*, 5911–5918.
[58] P. A. Zapata, J. Faria, M. P. Ruiz, R. E. Jentoft, D. E. Resasco, *J. Am. Chem. Soc.* **2012**, *134*, 8570–8578.
[59] W.-J. Zhou, L. Fang, Z. Y. Fan, B. Albela, L. Bonneviot, F. De Campo, M. Pera-Titus, J.-M. Clacens, *J. Am. Chem. Soc.* **2014**, *136*, 4869–4872.
[60] Z. Y. Fan, A. Tay, M. Pera-Titus, W.-J. Zhou, S. Benhabbari, X. Feng, G. Malcouronne, L. Bonneviot, F. De Campo, L. Wang, J.-M. Clacens, *J. Colloid Interface Sci.* **2014**, *427*, 80–90.
[61] W. Li, F. Ma, F. Su, L. Ma, S. Zhang, Y. Guo, *ChemSusChem* **2011**, *4*, 744–756.
[62] A. Khalafi-Nezhad, S. M. Haghighi, F. Panahi, *ACS Sustainable Chem. Eng.* **2013**, *1*, 1015–1023.
[63] G. Nawaratna, S. D. Fernando, S. Adhikari, *Energy Fuels* **2010**, *24*, 4123–4129.
[64] a) X. Yang, X. Wang, J. Qiu, *Appl. Catal. A* **2010**, *382*, 131–137; b) C. Yu, L. Fan, J. Yang, Y. Shan, J. Qiu, *Chem. Eur. J.* **2013**, *19*, 16192–16195.
[65] H. Tan, P. Zhang, L. Wang, D. Yang, K. Zhou, *Chem. Commun.* **2011**, *47*, 11903–11905.
[66] a) I. F. Teixeira, A. A. S. Oliveira, T. Christofani, F. C. C. Moura, *J. Mater. Chem. A* **2013**, *1*, 10203–10208; b) A. A. S. Oliveira, I. F. Teixeira, L. P. Ribeiro, E. Lorençon, J. D. Ardisson, L. Fernandez-Outon, W. A. A. MacEdo, F. C. C. Moura, *Appl. Catal. A* **2013**, *456*, 126–134; c) A. A. S. Oliveira, I. F. Teixeira, T. Christofani, J. C. Tristao, I. R. Guimaraes, F. C. C. Moura, *Appl. Catal. B* **2014**, *144*, 144–151.
[67] L. C. A. de Oliveira, N. T. Costa, J. R. Pliego, A. C. Silva, P. P. Souza, P. S. D. Patricio, *Appl. Catal. B* **2014**, *147*, 43–48.
[68] J. Zhang, A. Wang, Y. Wang, H. Wang, J. Gui, *Chem. Eng. J.* **2014**, *245*, 65–70.
[69] W. Zhai, G. Li, P. Yu, L. Yang, L. Mao, *J. Phys. Chem. C* **2013**, *117*, 15183–15191.
[70] a) M. F. Nsib, A. Maayoufi, M. Moussa, N. Tarhouni, A. Massouri, A. Houas, Y. Chevalier, *J. Photochem. Photobiol. A* **2013**, *251*, 10–17; b) T. Nakato, H. Ueda, S. Hashimoto, R. Terao, M. Kameyama, E. Mouri, *ACS Appl. Mater. Interfaces* **2012**, *4*, 4338–4347.
[71] W. Wua, S. Gao, W. Tu, J. Chen, P. Zhang, *Particuology* **2010**, *8*, 453–457.
[72] L. Leclercq, A. Mouret, A. Proust, V. Schmitt, P. Bauduin, J-M. Aubry, V. Nardello-Rataj, *Chem. Eur. J.* **2012**, *18*, 14352–14358.
[73] Y. Leng, J. Wu, P. Jiang, J. Wang, *Catal. Sci. Technol.* **2014**, *4*, 1293–1300.
[74] W. Q. Yizhan, W. W. Li, L. Wu, *Chem. Eur. J.* **2010**, *16*, 1068–1078.
[75] Z. Zheng, J. Wang, H. Chen, L. Feng, R. Jing, M. Lu, B. Hu, J. Ji, *ChemCatChem* **2014**, *6*, 1626–1634.
[76] a) Y. He, F. Wu, X. Sun, R. Li, Y. Guo, C. Li, L. Zhang, F. Xing, W. Wang, J. Gao, *ACS Appl. Mater. Interfaces* **2013**, *5*, 4843–4855; b) M. Tang, X. Wang, F. Wu, Y. Liu, S. Zhang, X. Pang, X. Li, H. Qiu, *Carbon* **2014**, *71*, 238–248.
[77] H. Yang, T. Zhou, W. Zhang, *Angew. Chem. Int. Ed.* **2013**, *52*, 7455–7459; *Angew. Chem.* **2013**, *125*, 7603–7607.
[78] W. Zhang, L. Fu, H. Yang, *ChemSusChem* **2014**, *7*, 391–396.
[79] a) X. Xu, Y. Li, Y. Gong, P. Zhang, H. Li, Y. Wang, *J. Am. Chem. Soc.* **2012**, *134*, 16987–16990; b) Z. Zhu, H. Tan, J. Wang, S. Yu, K. Zhou, *Green Chem.* **2014**, *16*, 2636–2643.
[80] X. Yang, Y. Liang, Y. Cheng, W. Song, X. Wang, Z. Wang, J. Qiu, *Catal. Commun.* **2014**, *47*, 28–31.
[81] P. A. Zapata, J. Faria, M. P. Ruiz, D. E. Resasco, *Top. Catal.* **2012**, *55*, 38–52.
[82] a) J. Faria, M. P. Ruiz, D. E. Resasco, *Adv. Synth. Catal.* **2010**, *352*, 2359–2364; b) M. P. Ruiz, J. Faria, M. Shen, S. Drexler, T. Prasomsri, D. E. Resasco, *ChemSusChem* **2011**, *4*, 964–974.
[83] a) S. Drexler, J. Faria, M. P. Ruiz, J. H. Harwell, D. E. Resasco, *Energy Fuels* **2012**, *26*, 2231–2241; b) D. Shi, J. A. Faria, A. A. Rownaghi, R. L. Huhnke, D. E. Resasco, *Energy Fuels* **2013**, *27*, 6118–6124.
[84] J. Liu, G. Lan, J. Peng, Y. Li, C. Li, Q. Yang, *Chem. Commun.* **2013**, *49*, 9558–9560.
[85] Y. Jiang, X. Liu, Y. Chen, L. Zhou, Y. He, L. Ma, J. Gao, *Bioresour. Technol.* **2014**, *153*, 278–283.
[86] C. Hou, H. Zhu, D. Wu, Y. Li, K. Hou, Y. Jiang, Y. Li, *Process Biochem.* **2014**, *49*, 244–249.
[87] Y. Yu, L. Fu, F. Zhang, T. Zhou, H. Yang, *ChemPhysChem* **2014**, *15*, 841–848.