### Pickering interfacial catalysis for organic synthesis

### A hotbed for innovation

Abstract Reactions between immiscible reagents in the presence of solid catalysts (liquid-liquid-solid, L-L-S reactions) are extensively used in the chemical industry. However, conventional reactors such as stirred tanks can suffer from strong mass/heat transfer limitations due to the poor contact between the phases and a reduced accessibility of the reactants to the catalyst surface. For a major improvement on current systems in terms of cost efficiency, energy savings and environmental footprint, L-L-S reactors operating at the nanoscale are required. Recently, we have reported the Pickering interfacial catalysis (PIC) concept. It addresses the reaction between two immiscible reagents by the formation of L-L-S nanoreactors based on Pickering emulsions promoting the contact between the phases. This paper presents an overview of recent examples of PIC systems developed at the E2P2L Laboratory in Shanghai and applied to industrially relevant reactions encompassing biomass-derived reagents for which reactivity is usually imprisoned due to low miscibility of the reagents. The PIC concept constitutes a hotbed for innovation, opening an avenue to the industrial synthesis of high added-value fine chemicals, specialties and biofuels that can only be afforded today using inefficient processes.

Keywords Biomass, multiphasic reactor, Pickering interfacial catalysis, emulsion, amphiphilic catalyst.

Résumé Catalyse interfaciale de « Pickering » pour la synthèse organique : une approche hautement innovante Les réactions entre composés non miscibles en présence de catalyseurs solides (réactions liquide-liquide-solide, L-L-S) sont très courantes dans l'industrie chimique. Néanmoins, l'utilisation des réacteurs conventionnels tels que les réacteurs mélangés peut être limitée par des phénomènes de transfert de matière et de chaleur en raison du faible contact entre les phases liquides et d'une accessibilité réduite des réactifs vers la surface du catalyseur. Afin d'améliorer la performance des réacteurs multiphasiques actuels en termes de rapport coût/efficacité, d'économie d'énergie et d'empreinte environnementale, il a paru souhaitable de développer des réacteurs L-L-S fonctionnant à l'échelle nanométrique. Récemment, nous avons mis en avant un concept alternatif dénommé « catalyse interfaciale de Pickering » (« Pickering Interfacial Catalysis », PIC). Il s'agit de favoriser la réaction entre les deux substrats non miscibles moyennant la formation de nanoréacteurs L-L-S basés sur des émulsions de Pickering, ce qui permet un contact accru entre les phases. Cet article présente un aperçu des avancées les plus récentes développées au Laboratoire E2P2L de Shanghai autour du concept PIC et visant des réactions à fort intérêt industriel utilisant des réactifs biosourcés pour lesquels les réactions sont difficiles pour des questions de miscibilité. Ce concept est particulièrement innovant ; il ouvre de nombreuses perspectives pour la synthèse à l'échelle industrielle d'une vaste gamme de produits de chimie fine et de spécialité, ainsi que des biocarburants, lesquels sont préparés aujourd'hui via des procédés peu efficaces.

Mots-clés Biomasse, réacteur multiphasique, catalyse interfaciale de « Pickering », émulsion, catalyseur amphiphile.

# Reengineering multiphasic reactors for L-L-S reactions

The production of chemicals and fuels using bio-based reagents is critical for a real conversion of the chemical industry towards sustainability and for warranting a transition to a circular economy [1-2]. In this context, immiscibility between the reactants is common [3]. Most often, organic solvents are used for boosting the miscibility of the reactants and conditioning the catalytic activity, which also favors in some cases product separation and catalyst recovery [4]. Nonetheless, solvents (including water) require further extraction/purification steps for recovery and reuse, hampering the economy and green footprint of the processes. Indeed, solvents contribute to 80% and 50% of the mass and energy utilization in chemical transformations, respectively, and their consumption is expected to grow at an annual rate of 2.5% until 2019 [5]. To develop greener and more sustainable processes, the design of solvent-free multiphasic reactions encompassing bio-based reagents appears as an urgent need.

When molecules A in the liquid phase L1 and B in the liquid phase L2 (L1 and L2 being not miscible) are to be reacted in the

presence of a solid catalyst (S), the overall reaction rate of the L-L-S system can be strongly decreased by two phenomena: the low mutual solubility of the reagents between both L1 and L2 liquid phases, and external mass/heat transfer, which is ascribed to the diffusion of reactants and products between both liquid phases and from each liquid phase to the catalyst surface. As a result, the overall reaction rate can be much lower (even null) than the intrinsic reaction rate that might be expected from the catalytic activity.

Common strategies for conducting L-L-S reactions encompass the use of surfactants and phase-transfer catalysts (*e.g.*, quaternary ammonium and phosphonium salts or crown ethers) for increasing the interfacial contact and distributing the catalyst between the phases [6]. Despite their potential benefits, surfactants and phase-transfer catalysts can be hardly recycled, affecting unavoidably the economy and eco-efficiency of the processes. Herein, after describing the main characteristics of conventional multiphasic reactors, including continuous flow microreactors and membrane contactors, we propose the design of novel L-L-S nanoreactors for conducting reactions at mild conditions. These unique systems can be foreseen as a platform for reengineering the already established multiphasic



Figure 1 - Multiphasic reactors for running L-L-S catalyzed reactions: (A) conventional reactor, (B) continuous flow microreactor, (C) catalytic membrane contactor, and (D) L-L-S nanoreactors based on Pickering emulsions.

reactors, exhibiting enhanced catalytic properties *via* a refined design of the triphasic contact at the nanoscale. As a result, major improvements in terms of cost efficiency, energy savings and environmental footprint are foreseen.

#### **L-L-S reactors**

Before starting our description of L-L-S nanoreactors, let us recall the different types of reactors for conducting L-L-S reactions. These can be broadly classified in the three main families with an increasing L-L-S contact: (A) conventional reactors, (B) continuous flow microreactors, and (C) catalytic membrane contactors (*figure 1*).

#### **Conventional reactors**

Conventional L-L-S catalytic reactors comprise slurry reactors (*e.g.*, stirred tanks, *figure 1A*) operated in batch, semi-batch or continuous mode, and to a minor extent packed beds [7]. Slurry reactors offer simple reactor geometries, efficient heat removal and high effectiveness factors for porous catalysts due

to their relatively lower particle sizes, but might present some drawbacks ascribed to catalyst filtration and attrition. As a rule, stirred tanks can suffer from low L-L and L-S interfacial areas  $(10^2-10^3 \text{ m}^2/\text{m}^3)$ , encompassing mass transfer coefficients in the range  $10^{-5}$ -5 s<sup>-1</sup> [8].

#### **Continuous flow microreactors**

Continuous flow microreactors (*figure 1B*) consist of small channels ( $\phi = 50-1000 \,\mu$ m) enabling larger interfacial areas ( $10^3 - 10^5 \,\text{m}^2/\text{m}^3$ ) and efficient L-L mixing and shorter diffusion paths, resulting in mass transfer coefficients in the range 3-8 s<sup>-1</sup>. Examples include catalyst-coated monoliths, stainless steel, silicon or oxidized aluminum wafers and platelets, glass chips and microcapillary reactors [9]. However, these reactors suffer from particle clogging, pulsating flows when using mechanical pumping and corrosion. Moreover, despite their modular architecture, up-scaling is not straightforward, which explains why to date no large-scale process based on microreactors has been developed and commercialized.

#### Catalytic membrane contactors

Catalytic membrane contactors coupling a catalyst and a hierarchical mesoporous membrane ( $\phi = 5-100$  nm) have been developed (*figure 1C*) [10]. This leads to a better accessibility of the reactants to the catalyst zone and in its turn to enhanced reaction rates at relatively mild temperature. Despite these benefits, catalytic membrane contactors are conditioned by the high cost of membranes, as well by their quality in terms of large-pore defects, preventing their industrial-scale implementation.

#### **L-L-S nanoreactors**

To overcome the intrinsic shortcomings of state-of-the-art multiphasic reactors, L-L-S reactors operating at the nanoscale could be a good option. In this view, surfactant-combined catalysts have been recently developed enhancing the interfacial surface area by the formation of amphiphilic supramolecular assemblies (*i.e.*, micelles, microemulsions, macroemulsions), boosting mass transfer between the phases [11]. Despite these potential benefits, surfactant-combined catalysts can be hardly recycled.

In addition to surfactants, colloidal nanoparticles (NPs) with amphiphilic properties can stabilize macroemulsions (also termed as Pickering emulsions), offering a platform for engineering catalytic L-L-S nanoreactors (figure 1D) [12]. Pickering emulsions are used today in a broad variety of fields including pharmaceutics, drug delivery and enhanced oil recovery (EOR). Besides, many food products used in our daily life (e.g., mayonnaise, margarine, ice-cream) are stabilized by sub-micron colloidal nanoparticles such as CaCO<sub>3</sub>, ethyl cellulose, proteinpolysaccharide complexes and fat crystals [13]. Unlike microemulsions, which occur spontaneously upon mixing the liquid phases and the surfactant, Pickering emulsions arise from the self-assembly of NPs at the liquid-liquid interface, generating a dense and rigid film that acts as a mechanical barrier against coalescence [12, 14]. As a result, Pickering emulsions can provide large interfacial contact areas and short diffusion paths, allowing fast mass/heat transfer between the phases. This property is of significance for designing L-L-S nanoreactors for reactions between immiscible reagents.

Despite their morphological differences, Pickering emulsions show analogies to catalytic membrane contactors with small pore sizes (< 10 nm). Indeed, in the latter, a hierarchical mesoporous membrane supporting the catalyst acts as an interfacial contactor between the reactants and the catalyst at the nanoscale. The accessibility of the reactants to the catalyst zone is promoted, leading to enhanced reaction rates at relatively mild temperature. In both cases, a narrow catalytic zone with a volume in the range 10-100 nm<sup>3</sup> can be generated, intensifying the contact at the nanoscale (compare figures 1D and 1C). The main difference between these concepts relies on the fact that a membrane is required in catalytic membrane reactors to generate the interfacial contact area, whereas in Pickering emulsions the amphiphilic particles adsorb and interact one another at the L-L interface, generating a "selfassembled membrane".

The application of Pickering emulsions to the field of catalysis can be conducted in two different ways (*figure 2*):

- *Pickering Assisted Catalysis* (PAC), where a homogeneous catalyst or enzyme can be combined with amphiphilic NPs, colloidosomes, polymersomes or microgels located either in the dispersed or continuous phases [15];

Catalytic zone



Figure 2 - Comparison between Pickering Assisted Catalysis (PAC) (top) and Pickering Interfacial Catalysis (PIC) (bottom) for conducting L-L-S reactions. In PAC, the catalyst (green squares) is located preferentially in one of the bulk phases, whereas in PIC, the catalyst is self-assembled at the L-L interface.

- Pickering Interfacial Catalysis (PIC), where the NPs behave concomitantly as solid emulsifiers and interfacial catalysts. The latter concept has recently become a hot topic, since heterogeneous catalysts can be re-engineered for decreasing mass transfer resistances in L-L-S reactions [16]. Furthermore, the reactivity can be locally conditioned by unique nanoscopic properties ascribed to L/L interfaces, such as interfacial acidification, preferential molecular orientation and enhanced miscibility [17]. In the following lines, we provide an overview of PIC systems developed by our team for conducting L-L-S reactions for the synthesis of bio-based products.

#### Examples of L-L-S nanoreactors developed at E2P2L

For the genesis of nanoreactors for conducting L-L-S reactions under the PIC principle, it is crucial to render amphiphilic the catalytic NPs by adjusting the hydrophilic-lipophilic balance. Besides, the NP size and NP loading are important factors for building self-assembled membranes at the liquide-liquide interface. The membrane architecture conditions the available contact area and diffusion path of reactants and products near the catalytic centers. As a result, specific NPs need to be designed and engineered for a given reaction, as further shown.

#### Acetalization reactions

As a proof of the validity of the PIC concept, we reported the design of amphiphilic silica NPs incorporating propylsulfonic acid groups and octyl and octadecyl chains for conducting the acid-catalyzed acetalization reaction of dodecanal with ethylene glycol (EG) for the production of bio-based fuels (*figure 3, left*) [18]. The silica NPs were prepared by coprecipitation and displayed an average particle size in the range of 150-300 nm with a high density of alkyl chains and



Figure 3 - Left: acid-catalyzed acetalization of fatty aldehydes with EG catalyzed by amphiphilic silica NPs incorporating propylsulfonic acid groups (brown-red), silanol groups (blue) and octadecyl chains (pink). Right: microscopic images of dodecanal/EG emulsions (50:50 v/v) in the presence of the NPs (1.7 wt.% with respect to both reagents) at room temperature after 5 days, and macroscopic appearance of dodecanal/EG emulsions just after multiple emulsification tests. Reaction conditions: 60°C, dodecanal (10 mmol), EG (20 mmol), catalyst (1.7 wt.% with respect to both reagents or 9.5 µmol H<sup>+</sup>). Images adapted from [18].



Figure 4 - Left: scheme of the PIC concept applied to the preparation of ethoxylated surfactants from glycerol and dodecanol. Right: macroscopic and 2D confocal fluorescence images of D/G/D double Pickering emulsions over sulfonated polystyrene-grafted silica NPs with 28% grafting degree. Reaction conditions: 150°C, 24h, dodecanol (6.45 mmol), glycerol (25.5 mmol), catalyst (2 wt.% with respect to both reagents), static vacuum, homogenization at 45°C for 2 min and 13,000 rpm. Images adapted from [21].

silanol groups (> 20 alkyl groups/nm<sup>2</sup> and > 33 SiOH/nm<sup>2</sup> for octadecyl functionalized silica). The reaction progressed faster in the presence of amphiphilic silicas, reaching chemical equilibrium after 1h at 60°C. The same reaction performed using p-toluenesulfonic acid (PTSA) and benchmark catalysts such as acid resins and HZSM-5 with the same number of acid equivalents (9.5 µmol) was much slower. The enhanced activity was ascribed to the formation of stable dodecanal/EG Pickering emulsions (*figure 3, right*), favoring the contact and mass transfer between the reagents. The catalysts could be recovered by centrifugation after reaction and reused with no deactivation after 7 consecutive runs.

#### **Etherification reactions**

In a further extension of the PIC concept, we tackled the synthesis of novel ethoxylated surfactants (DGE) from the direct reaction of glycerol with dodecanol (*figure 4A*). This is a very challenging reaction for which very few examples have been reported in the literature [11a, 19]. Glycerol is a highly viscous and polar liquid, whereas dodecanol is a fatty alcohol

with low viscosity which solidifies at room temperature. Even if dodecanol can be emulsified with water, the two components are poorly miscible up to 200°C even in the presence of solvents.

As a way out to this shortcoming, we designed amphiphilic silica NPs for the solvent-free etherification of glycerol (G) with dodecanol (D). Aerosil<sup>®</sup>200 silica NPs were grafted with propyl sulfonic acid groups and alkyl chains with variable length (C3, C8, C18). The average NP size was found in the 38-225 nm range. These NPs were able to stabilize G/D Pickering emulsions even at high temperature [20]. In all cases, the interfacial tension,  $\gamma$ , declined from 6.2 mN/m without NPs to 2.5 mN/m in the presence of Aerosil<sup>®</sup>200 silica NPs grafted with octadecyl chains. The modified silica NPs were able to activate the interfacial reaction of both reagents at 150°C, but the yield to the ethoxylated products remained low (< 10%). In contrast, the catalytic activity increased by a 30-fold factor compared to PTSA or propyl-grafted silica combined with PTSA.

In a following study, we prepared polystyrene-grafted silica NPs (average NP size = 45-80 nm) bearing sulfonic acid



Figure 5 - Left: principle of PIC system for the low-temperature acid-catalyzed biphasic hydrolysis of triglycerides into FFAs by amphiphilic Aquivion<sup>®</sup>. Right: GTL/water emulsions at 100°C after reaction. Reaction conditions: 100°C, 8h, GTL (0.15 mmol), water (16 mmol), catalyst (1 wt.% with respect to both reagents), homogenization at 70°C for 5 min and 20,000 rpm. Images adapted from [23].

centers. Their surface properties and molecular weight were made tunable by transfer radical polymerization (ATRP) of styrene on Aerosil®200 silica previously grafted with [(chloromethyl)phenylethyl] trimethoxysilane followed by sulfonation. The density of sulfonated polystyrene moieties evolved from 0.6 to 8.6 groups/nm<sup>2</sup> for longer-chain silicas with a molecular weight in the range 4900-8600 g/mol, while the density of SiOH groups was found in the narrow range 2.7-2.9 groups/nm<sup>2</sup>. By optimizing the hydrophobic properties of the NPs, D/G/D double Pickering emulsions could be stabilized at 150°C after 16h at 2 wt.% NP loading due to the presence of a G/D/NP contact angle approaching 90°. The formation of D/G/D double Pickering emulsions afforded a dispersion level of glycerol and dodecanol as high as 97% of the total volume with a glycerol average droplet size of only 2 µm (figure 4). This resulted in a facilitated diffusion of glycerol and dodecanol into the microenvironment nearby the acid centers and in turn in an unprecedented yield (> 40%) towards the ethoxylated products (figure 4, left) [21].

#### Hydrolysis of triglycerides

Free fatty acids (FFAs) are major components in the synthesis of a great variety of products such as soaps, detergents, lubricants, paints, cosmetics, pharmaceuticals and food additives. Biodiesel can also be produced from fatty acids by esterification with methanol. FFAs are produced industrially by fat splitting (i.e. hydrolysis of triglycerides) either under superheated steam to promote water solubility, or by saponification with a strong base [22]. However, all these processes suffer from harsh reaction conditions (i.e. high temperature and pressure, strong acidity/basicity, use of surfactants), leading to thermal decomposition and corrosion, as well as to multiple steps for purification. As a greener alternative, solid acid catalysts operating at milder conditions have been proposed for the hydrolysis of vegetable oils and fats. However, as a rule, acid catalysts exhibit poor activity even at high temperature (150-350°C) due to resilient mass transfer limitations.

As a first attempt, we explored the activity of Aerosil®200 silica modified by grafting of propyl sulfonic groups and alkyl chains with variable length (from C3 to C8) on Aerosil®200 silica in the low-temperature hydrolysis of glyceryl trilaurate (GTL). At 100°C for 10h using a water excess, the different NPs were able to stabilize GTL/water emulsions, but none was active, even at high loading (*i.e.* 1 eqH<sup>+</sup> vs. GTL) [23]. However, a high activity was observed in the hydrolysis of glycerol monolaurate (GML) at low NP loading (2 wt.%) in the presence of Pickering emulsions (at 100°C for 10h). These results suggested that the acid strength was not suitable for performing the first step of GTL hydrolysis, which can be regarded as the rate-limiting reaction.

As an alternative, we explored the potentials of different fluorinated resins combining hydrophobic surface properties and stronger acidity than silicas for performing GTL hydrolysis at mild temperature (100°C) and ambient pressure (*figure 5*, *left*) [23]. The Aquivion® Perfluorosulfonic Superacid (PFSA, PW98) resin developed by Solvay Special Polymers was found very active for the reaction due to the formation of stable GTL/water Pickering emulsions that remained stable during the reaction (*figure 5*, *right*). Furthermore, Aquivion® could be immobilized in carbon during the hydrothermal carbonization of polysaccharides affording the preparation of Aquivion®-carbon composites with tunable hydrophilic/hydrophobic properties and easy recycling.

#### **Benzene hydroxylation**

Since the discovery of TS-1 in the 1980s, Ti-silicates have attracted great interest due to their outstanding catalytic properties in selective oxidation reactions using hydrogen peroxide as mild oxidant and organic solvents [24]. Very recently, we reported the preparation of amphiphilic titanosilicates for conducting the solvent-free biphasic hydroxylation of benzene with H<sub>2</sub>O<sub>2</sub> [25]. A partially hydrophobized coreshell TS-1@KCC (TK) (KCC = Kaust Catalysis Center) showed a higher catalytic activity compared to hydrophilic counterpart catalysts due to the formation of stable benzene/water Pickering emulsions (figure 6). At optimized conditions, TS-1@KCC-1 grafted with octyl and octadecyl chains (i.e. TK-0.5C8 and TK-2C<sub>18</sub>) afforded an interfacial activity of 1.1 mol.(Ti-mol)<sup>-1</sup> with an excellent stability and good reusability. A simulation study using dissipative particle dynamics (DPD) over coarse-grained alkyl grafted silicas confirmed the stabilizing effect of octyl chains for the benzene/water system [26].

#### What's next?

Along this paper, we have presented examples of L-L-S nanoreactors based on Pickering emulsions developed at the E2P2 Laboratory in Shanghai for conducting the reaction between immiscible reagents. The key to these systems is the design of amphiphilic nanoparticles behaving simultaneously as emulsifiers and catalysts for enhancing mass transfer between the phases. This novel technology can be in principle applied to boost the reactivity for a broad panel of biphasic systems encompassing especially bio-based reagents. The



Figure 6 - (A) Benzene hydroxylation over pristine TS-1, TK-xC<sub>n</sub>, where *x* refers the number of moles used for the grafting agent for 1 g sample and *n* the corresponding chain length. (B) TEM micrograph of TK-0.5C<sub>8</sub>. (C) Optical image of a benzene/water emulsion stabilized by TK-0.5C<sub>8</sub>. Reaction conditions:  $60^{\circ}$ C, 1h, benzene (17 mmol), water (79 mmol), H<sub>2</sub>O<sub>2</sub> (30 wt.%), catalyst (1.8 wt.% with respect to both reagents), homogenization at room temperature for 3 min and 16,000 rpm. Images adapted from [25].



L'équipe du laboratoire E2P2 à Shanghai, juin 2018.

next steps are to achieve proper upscaling and process design, for which challenges such as particle separation and recycling need to be circumvented.

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