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Pickering emulsions as compartmentalized reaction media for catalysis

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PURPOSE OF THE ABSTRACT

Compartmentalization is a very effective method to deal with chemical complexity. Nature, for example uses cell membranes to physically separate chemically incompatible reagents to perform multiple reactions simultaneously. Here, we report on synthetic compartmentalization of (antagonistic) catalysts using Pickering emulsions (PEs), emulsions stabilized by solid particles, and explore the properties of these emulsions in catalysis. This strategy offers opportunities for process intensification and a more efficient and greener conversion of renewables. Water-in-oil emulsions formulated with the lignin-derived organic solvents 2-isopropylphenol (IPP), 4-propylguaiacol (PG) and 2-sec-butylphenol (SBP) and stabilized by fumed silica are reported for the first time. As most of the few reported applications of PE in catalysis typically involve very mild reaction conditions and do not focus on stability of PEs under reaction conditions, their broader applicability remains to be established. The stability of the emulsions and hence the window of operation for catalytic conversion was therefore studied at high temperature, salt and acid concentrations, to mimic typical conditions of, for example, biorefinery operations. The PG based emulsions proved most stable, tolerating salt (NaCl) concentrations up to 30 wt% and a pH of 1.3 for over a month. This PE can also withstand temperatures up to 100 °C, the boiling point of the dispersed phase.

An increase of interfacial area and the ability for compartmentalization with a physical boundary between the two phases, are two of the benefits that PEs offer over traditional biphasic systems that can be useful in catalysis. For example, we show by kinetic studies that the lignin-derived PEs show good potential for the extraction of HMF (figure 1a) generated by acid-catalysis from fructose, a reaction for which rapid extraction from the water phase is required to obtain good yields.

Taking advantage of both the increased interfacial area and the physical boundary, we show that PEs can serve as reaction media for tandem reactions with antagonistic catalysts. This is highlighted for tandem acid-base catalysis using the deacetalization-Knoevenagel probe reaction. In this case, the acid and base catalysts are compartmentalized in the water and organic phases of the PE, respectively, avoiding the immediate quenching of the acid and base catalysts that would otherwise occur (figure 1b).

Finally, we show that confining a catalyst in the dispersed phase and substrates and products in the continuous phase of a PE offers the potential of heterogenization of a homogeneous catalyst and of continuous flow, using a microfluidics approach or the equivalent of a fixed bed reactor used in heterogeneous catalysis. Together the results show that PE can be attractive media for catalysis and the more sustainable production of chemical building blocks.

FIGURES

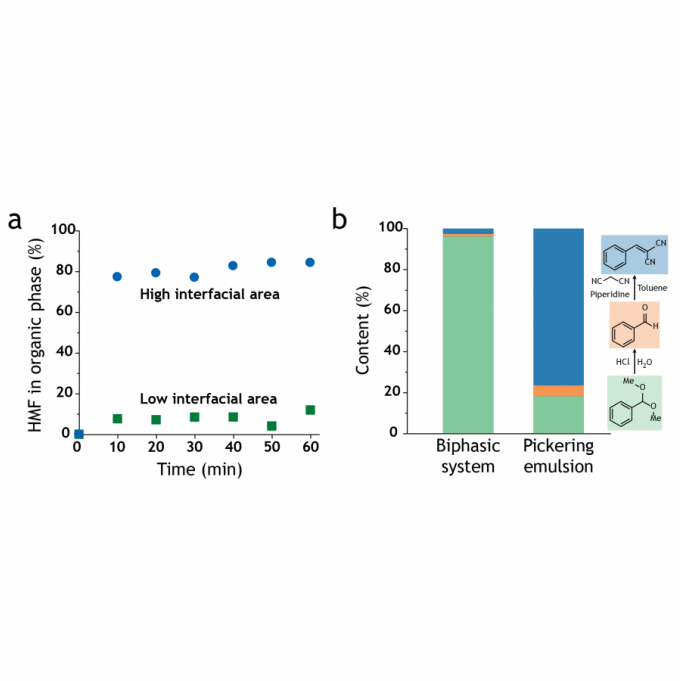

FIGURE 1

Figure 1

a) Influence of interfacial area of biphasic systems on the extraction kinetics of HMF from water to the lignin-derived organic solvents. b) Performance of a traditional biphasic system and PE in the acid-base catalyzed deacetalization-Knoevenagel reactio

FIGURE 2

KEYWORDS

Pickering emulsions | Biphasic catalysis | Biobased solvents | Process internsification

BIBLIOGRAPHY