

N°727 / OC

TOPIC(s) : Clean reactions / Alternative technologies

## Pickering Interfacial Catalysis for the Oxidative Cleavage of Cyclohexene: A Novel and Green Approach for the Synthesis of Dicarboxylic Acids

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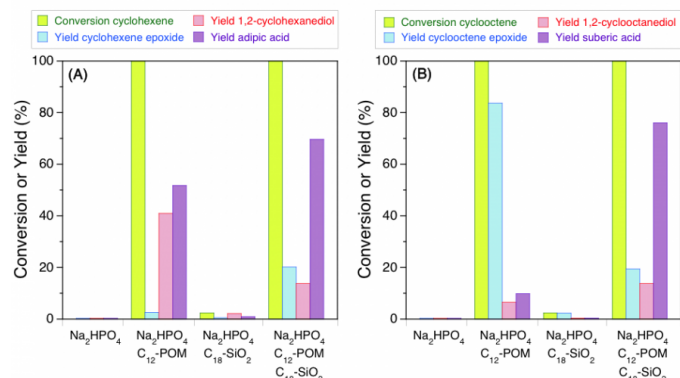
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### PURPOSE OF THE ABSTRACT

Adipic acid, mainly used as an intermediate for the production of Nylon 6,6, is the most important dicarboxylic acid. The most extended process for the synthesis of adipic acid involves the oxidation of a mixture of cyclohexanol and cyclohexanone (KA oil) with nitric acid. This process is clearly incompatible with the Green Chemistry principles, since it generates a greenhouse gas (N<sub>2</sub>O) as by-product and large amounts of salt. 1 As an alternative, Sato et al. designed a cleaner strategy to produce adipic acid by the oxidative cleavage of cyclohexene using hydrogen peroxide as an oxidant, a phase transfer catalyst (i.e. quaternary ammonium salts) and sodium tungstate as catalyst.2 Despite its benefits, this process uses a homogeneous catalyst, which can be hardly recycled, and suffers from a low contact between the organic and aqueous phases, mitigating the catalytic activity.

Pickering Interfacial Catalysis (PIC) has recently emerged as a potential solution for overcoming such limitations. In this concept, the reagents are emulsified by solid amphiphilic catalysts, generating a large interfacial surface area that accelerates mass transfer.3 Herein, we present for the implementation of the PIC concept to the design of catalytic cascades at the water/oil interface. As a marking example, we conducted the oxidative cleavage of cyclohexene and cyclooctene to adipic and suberic acids, respectively, in the presence of Pickering emulsions using H<sub>2</sub>O<sub>2</sub> as an oxidant. The emulsions were stabilized by amphiphilic [C12]<sub>3</sub>[PW12O<sub>40</sub>] (C12-POM) and [C18/C3SO<sub>3</sub>H]@SiO<sub>2</sub> (C18-SiO<sub>2</sub>) nanoparticles (NPs) with oxidation and acid properties, respectively, assembling at the oil/water interface. Besides, two phosphate additives were used as co-catalysts for accelerating the epoxidation reaction, namely the surfactant-like [C12][H<sub>2</sub>PO<sub>4</sub>] and the Na<sub>2</sub>HPO<sub>4</sub> salt being solubilized in the aqueous phase. In the former case, the C18-SiO<sub>2</sub> NPs did not exert a significant effect on the catalytic properties due to the preferential adsorption of [C12][H<sub>2</sub>PO<sub>4</sub>] at the oil/water interface, catalysing the hydrolysis steps. In contrast, a neat effect of C18-SiO<sub>2</sub> NPs was observed on the catalytic properties, which was more apparent for cyclooctene due to its higher hydrophobic properties compared to cyclohexene, making it less accessible to the interface (Figure 1).

## FIGURES



**FIGURE 1**

Figure 1

Oxidative cleavage of (A) cyclohexene and (B) cyclooctene. Reaction conditions: 0.75 mL toluene (2 mol/L cyclohexene or cyclooctene), 2.25 mL H<sub>2</sub>O (1.2 equiv. H<sub>2</sub>O<sub>2</sub>), 50 mg C<sub>12</sub>-POM, 50 mg C<sub>18</sub>-SiO<sub>2</sub>, 2 equiv. Na<sub>2</sub>HPO<sub>4</sub> with respect to C<sub>12</sub>-POM, 60 °C, 500 rpm. 4

**FIGURE 2**

## KEYWORDS

Adipic Acid | Oxidative Cleavage | Pickering Emulsion | Catalytic Cascade

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