

Pickering Interfacial Cascade Catalysis of Cyclohexene Epoxide: A Novel and Green Approach for the Synthesis of Dicarboxylic Acids

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Abstract: Organic syntheses using biomass-derived reagents usually encompass the reaction of immiscible reagents showing low catalytic activity due to resilient mass transfer limitations. *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. Herein, we present for the first time the implementation of the PIC concept to the design of catalytic cascades at the water/oil interface (i.e. Pickering Interfacial Cascade Catalysis, PICC). As a marking example, we conducted the oxidative cleavage of cyclohexene epoxide using H₂O₂ as an oxidant, targeting the synthesis of diacids. To this aim, we design amphiphilic nanoparticles based on polyoxometalates and acid silicas that were able to assemble together at the water/oil interface, affording a synergistic effect on the stabilization of Pickering emulsions, and accordingly on activating the catalytic cascade.

Keywords: Pickering Interfacial Catalysis (PIC), Oxidative cleavage, Colloidal Chemistry.

1. Introduction

Adipic acid is an important commodity used for the production of Nylon 6,6. The industrial production of adipic acid involves the oxidation of a mixture of cyclohexanol and cyclohexanone (KA oil) with nitric acid. This process generates large amounts of greenhouse gases (N₂O), as well as harmful wastewater. Inspired by the concept of “Green Chemistry”, Sato *et al.*¹ designed a cleaner strategy to produce dicarboxylic acids by the catalytic oxidative cleavage of cyclohexene, encompassing the use of sodium tungstate as catalyst assisted by a phase transfer catalyst (PTC) and H₂O₂ as an oxidant. Despite its benefits, the low contact between the organic and aqueous phases remains an important challenge to promote the catalytic activity.

Very recently, *Pickering Interfacial Catalysis* (PIC) has emerged as a potential solution for conducting biphasic reactions with immiscible reagents.² Indeed, Pickering emulsions stabilized by solid nanoparticles (NPs), allow the dispersion of both phases with high stability against coalescence. When the amphiphilic solid NPs also act as a catalyst, then the reaction occurs at the water/oil interface with remarkable efficiency. Herein, amphiphilic alkyl polyoxometalates (POMs) ([C₁₂]₃[PW₁₂O₄₀]) and silica NPs grafted with alkyl and acid sites (80/20 C₁₈/C₃SO₃H) were prepared, showing a pronounced synergistic effect in the stabilization of Pickering emulsions. Relying on this property, an acid-redox catalytic cascade was designed, affording the oxidative cleavage of cyclohexene epoxide with H₂O₂ at the oil/water interface without any additive.

2. Experimental

The amphiphilic POM NPs ($\phi = 50$ nm) were prepared by reaction of dodecyltrimethylammonium bromide previously exchanged with HO⁻ groups with tungstophosphoric acid.³ Besides, the amphiphilic silica NPs were prepared by grafting propylsulfonic acid sites and inert alkyl chains (i.e. propyl, octyl, octadecyl) with variable proportion on Aerosil[®]200 fumed silica by silylation.⁴ Water/toluene emulsions using each family of NPs either individually or combined were stabilized at 60 °C without stirring. In these tests, 0.1 g (3.6 wt.%) NPs, 1.5 mL toluene and 1.5 mL water were emulsified with an Ultra-Turrax[®] at 11,500 rpm for 1 min. The oxidative cleavage of cyclohexene epoxide was carried out using the same biphasic system using 0.5 M cyclohexene epoxide and 3.5 equiv. H₂O₂ in the toluene and water phases, respectively. The reaction was conducted at 80 °C, 500 rpm for 12 h. The reaction products were analyzed by GC and ¹H NMR using DMSO as solvent and dodecanol as internal reference.

3. Results and discussion

In a first step, we studied the emulsification properties of the POM and acid silica NPs, either alone or combined (Figure 1). In all cases, a limited coalescence is observed, where the rate of coalescence slows down or even completely stops. This phenomenon is enhanced in the sense $[C_{12}]_3[PW_{12}O_{40}] < 80/20 C_{18}/C_3SO_3H < \text{mixed NPs}$. The dispersed volume and the emulsion stability are enhanced when both NPs are combined. These effects combined with a drastic decrease of the average droplet size favors the generation of contact area between the phases. The synergistic effect between both NPs can be attributed to interparticle hydrophobic forces between the alkyl chains, attaching firmly the NPs at the surface of the droplets.

Subsequently, we studied the catalytic properties of the different NPs, either combined or alone, in the oxidative cleavage of cyclohexene epoxide with H_2O_2 in the presence of Pickering emulsions (Table 1). In the absence of catalyst, the hydrolysis of cyclohexene epoxide occurred with 85% yield to the diol intermediate. A similar result was obtained when only amphiphilic silica NPs were used. When only $[C_{12}]_3[PW_{12}O_{40}]$ NPs are added to the system, the yield to adipic acid was 62%, favoring the oxidation of the diol. Finally, when both $[C_{12}]_3[PW_{12}O_{40}]$ and acid silica NPs were combined, a complete redox-acid cascade could be performed, affording the a yield to adipic acid of 93%.

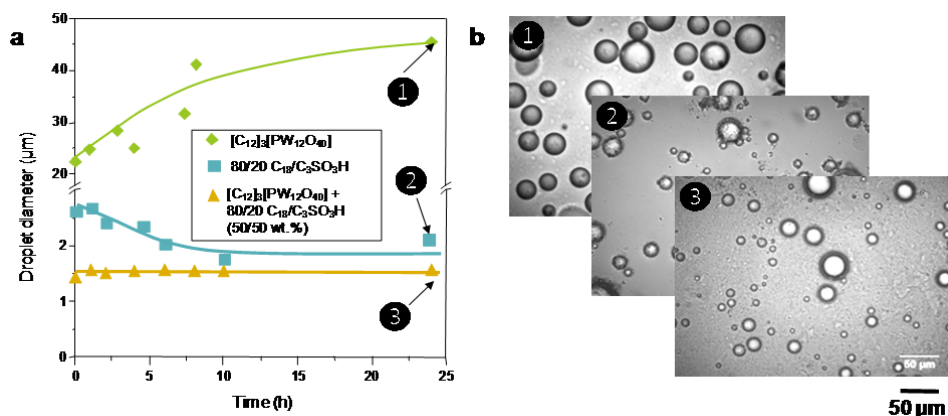


Figure 1. a) Droplet evolution (SD = 10%) and b) microscopic images of toluene/water emulsions stabilized by amphiphilic $[C_{12}]_3[PW_{12}O_{40}]$ NPs (1), amphiphilic acid silicas (80/20 C_{18}/C_3SO_3H) (2) and a 1 : 1 combination of both NPs. Conditions: 6 mL toluene, 6 mL water, 3.6 wt.% NPs, 60 °C, emulsification at 11,500 rpm for 8 min.

Table 1. Catalytic results for the oxidative cleavage of cyclohexene epoxide. ^a Measured by analyzing the aqueous phase; ^b Measured after fully extraction of the cleaved products

Catalysts	None	$[C_{12}]_3[PW_{12}O_{40}]$	80/20 C_{18}/C_3SO_3H	80/20 $C_{18}/C_3SO_3H + [C_{12}]_3[PW_{12}O_{40}]$ (1:1)
Yield of diol (%) ^a	85	31	81	5
Yield of adipic acid (%) ^b	6	62	13	93

4. Conclusions

By assembling two types of catalytic NPs at the water/oil interface, a pronounced synergistic effect of the NPs on the stabilization of Pickering emulsions was achieved. On the guidance of this effect, an efficient catalytic cascade for the biphasic reaction of cyclohexene epoxide with H_2O_2 in the presence of Pickering emulsions could be designed. This study opens up the possibility of designing eco-friendly catalytic cascades in biphasic media for industrially relevant reactions while complying with the Green Chemistry principles with respect to atom economy and the separation of the reaction product and the catalytic NPs.

References

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