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Pickering Interfacial Catalysis for Aerobic Alcohol Oxidation in Oil Foams

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PURPOSE OF THE ABSTRACT

Gas-liquid-solid (G-L-S) reactions are ubiquitous in catalytic processes. Conventional reactors such as packed beds (e.g., trickle beds, bubble columns) and stirred reactors typically suffer from low gas solubility in liquids, and resilient mass/heat transfer limitations, especially for fast reactions.1 In practice, co-solvents, surfactants, G-L phase-transfer reagents (e.g., molten salts) and high gas pressures are required to promote the G-L contact and increase the gas concentration, which affects the economy and green footprint of the processes.

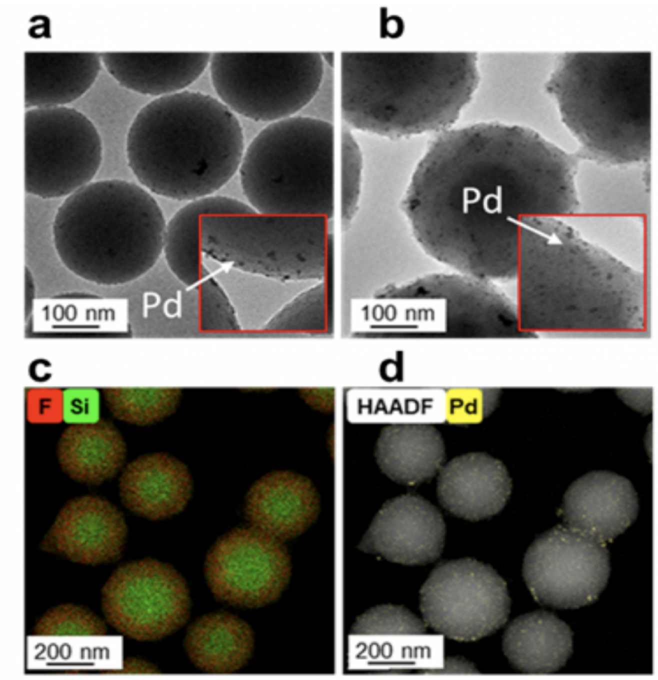
Pickering emulsions can be used to engineer catalytic reactions between two immiscible liquid reagents.2 Despite this progress, the transposition of Pickering emulsions to G-L systems based on ?armored? bubbles (e.g., foams) has been seldom explored, especially dealing with organic solvents, due to their low surface tension.3 Herein, we report the first example of an oil foam stabilized by surface-active oleophobic silica particles incorporating Pd nanoparticles able to catalyze the aerobic oxidation of alcohols at the air-oil interface.

We prepared fluorinated silica particles bearing catalytic sites for stabilizing foams and conducting interfacial reactions at the liquid-air interface. The mean particle size (HR-TEM) was in the range 364 for fluorinated Pd@SiNP_F17, whereas it was slightly smaller for Pd@SiNP_C8 particles (246 nm) (Figure 1). The Pd@SiNP_F17 particles consisted of a silica core and a fluorinated shell with a thickness increasing with the F loading.

We conducted the aerobic oxidation of benzyl alcohol as model reaction on the different particles using xylene as solvent. At low stirring rates (250-750 rpm), Pd@SiNP_C8 and Pd@SiNP_F17 particles show similar yet low catalytic performance (Figure 2b). At higher rates, the system with Pd@SiNP_F17 exhibits a sharp increase of the benzaldehyde (BnAH) yield after 1 h, whereas the yield remains almost unchanged for Pd@SiNP_C8. This large gap in catalytic activity between both particles is attributed to BnOH/xylene foam generation for Pd@SiNP_F17 at high stirring rates (Figure 2a,c,d). The BnAH yield increases monotonously at higher stirring rates (1000-1500 rpm) for Pd@SiNP_F17, which can be credited to an increase of foam volume.

We also studied the catalytic performance at variable particle concentration and 1500 rpm. For Pd@SiNP_C8, the BnAH yield lies below the detec-tion limit for 0.1-0.25wt% particle concentration, whereas it rises from 3% to 16% in the concentration range from 0.5wt% to 10wt%. In all cases, no foam is generated. In contrast, for Pd@SiNP_F17, the BnAH yield shows a volcano plot at a particle concentration about 1-2wt% affording the genesis of stable BnOH/xylene foams provided that the contact angle locates in the range 41-73°. At very low particle concentration, the foam is rather unstable, leading to low BnAH yield. At concentrations higher than 4 wt%, a majority of bubbles are covered by a close-packed layer of particles, resulting in very stable foams with a collapse time longer than the reaction time. This has a very important consequence: the O2 concentration becomes a limiting factor, as O2 in the bubbles cannot be regenerated. This body of results points out that intermediate particle concentrations are required to enhance the catalytic activity in oil foams, boosting the interfacial area while maintaining the permeability of the particle layer.

FIGURES



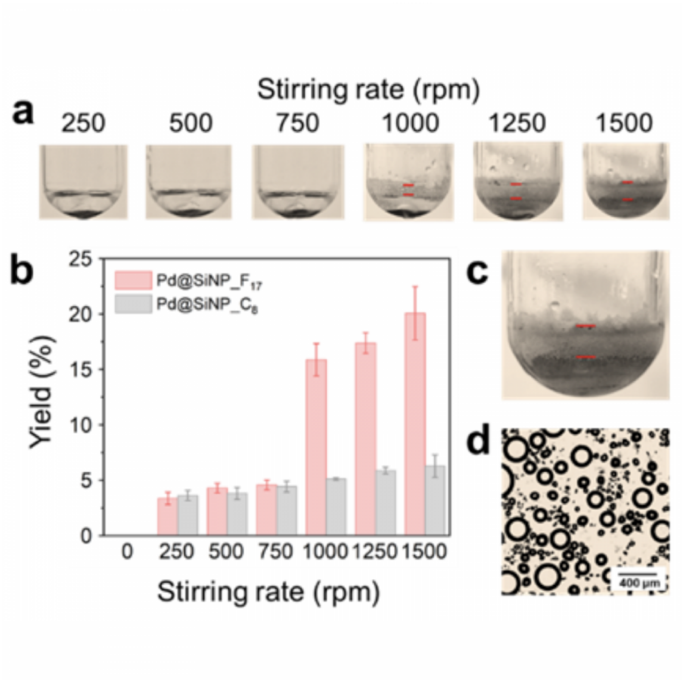


FIGURE 1

Figure 1.

(a) HR-TEM image of Pd@SiNP_C8. (b-d) HR-TEM/EDS micrographs of Pd@SiNP_F17.

FIGURE 2

Figure 2.

(a) Optical images of BnOH/Xylene as a function of stirring rate at 80 °C and 1 h. (b) Aerobic oxidation of BnOH over Pd@SiNP_C8 and Pd@SiNP_F17. (c) Zoom of BnOH/Xylene (1:1 v/v) system stabilized by 1wt% Pd@SiNP_F17 at 1500 rpm, 80 °C, 1 h. (d) Microsco

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KEYWORDS

Pickering Interfacial Catalysis | Foam | Surface-Active Particle | Aerobic Oxidation

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