Phase-Selective Catalysis in Emulsions Stabilized by Janus Silica-Nanoparticles

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Abstract: Metal-containing Janus particles are used as interfacial catalyst/emulsifiers that catalyze reactions in biphasic systems with controlled "*phase selectivity*", that is, conversion of the desired reaction on one side of the emulsion. The reaction may affect the solubility of the molecule in one phase, causing migration to the opposite phase. As a result, combined reaction and separation can be achieved in a single reaction vessel.

Keywords: emulsion catalysts; heterogeneous catalysis; Janus particles; phase selectivity; Pickering emulsions

We have recently shown that carbon nanotubes fused to oxide nanoparticles are able to stabilize emulsions and, when properly functionalized, catalyze reactions at the oil-water interface (i.e., liquid/solid/liquid interfacial catalysis).[1,2] To catalyze hydrodeoxygenation and etherification reactions, a noble metal was anchored to the surface of the nanohybrid, and to catalyze condensation reactions a solid basic function was incorporated. Although the use of interfacial catalysts has been reported in previous studies, they either used liquid surfactants to stabilize emulsions[3,4] or did not generate emulsions.[5] The advantage of the novel methodology is that the amphiphilic nanohybrids stabilize a high interfacial area, which results in higher conversions, and it does not require the use of a liquid surfactant that could not be separated from the reaction mixture. In contrast to homogeneous catalysts previously used, the recoverable solid stabilizes a water-in-oil emulsion and catalyzes reactions. This combination of heterogeneous and phase-transfer catalysis presents several advantages:[6] a) increased interfacial area, b) enhanced mass transfer of molecules between the two phases, c) simplified reaction/separation process by using a recoverable solid catalyst instead of surfactant, and d) effective separation of products from the reaction mixture by differences in the water-oil solubility (avoiding heating that leads to product decomposition).[2]

In this contribution, we explore the application of another class of amphiphilic material, the so-called Janus nanoparticles, as interfacial catalyst emulsifiers. The tunable surface properties of Janus nanoparticles have attracted attention for applications as diverse as sensing, electronics, photonics, and drug delivery.[7–12] Moreover, they can stabilize emulsions more efficiently than homogeneous solid particles.[13] The compartmentalized surface of Janus nanoparticles displays two opposite sides with different wettability, which are known to stabilize emulsions effectively.[14–20] Here, we have combined the concepts of two-phase catalysis and the surface compartmentalization to maximize "*phase selectivity*" of target reactions, that is, achieve conversion only on one side of the emulsion. As a proof-of-concept, we have conducted the phase-selective hydrogenation of an aldehyde dissolved in the organic phase, while avoiding reaction of another aldehyde dissolved in the aqueous phase, a process with potential application in biofuel refining.[21]

In our previous report, we demonstrated the concept of phase-selective catalysis in the aqueous phase of a biphasic system.[2] In that case, we used Pd clusters deposited on the hydrophilic side of nanohybrids composed of carbon nanotubes and silica oxide. We indicated that it is challenging to selectively deposit a metal on the hydrophobic side because pristine nanotubes do not anchor metal particles as effectively as the oxide supports. Therefore, one of the goals of the present work is to achieve phase selectivity in the organic phase, without conversion in the aqueous phase.
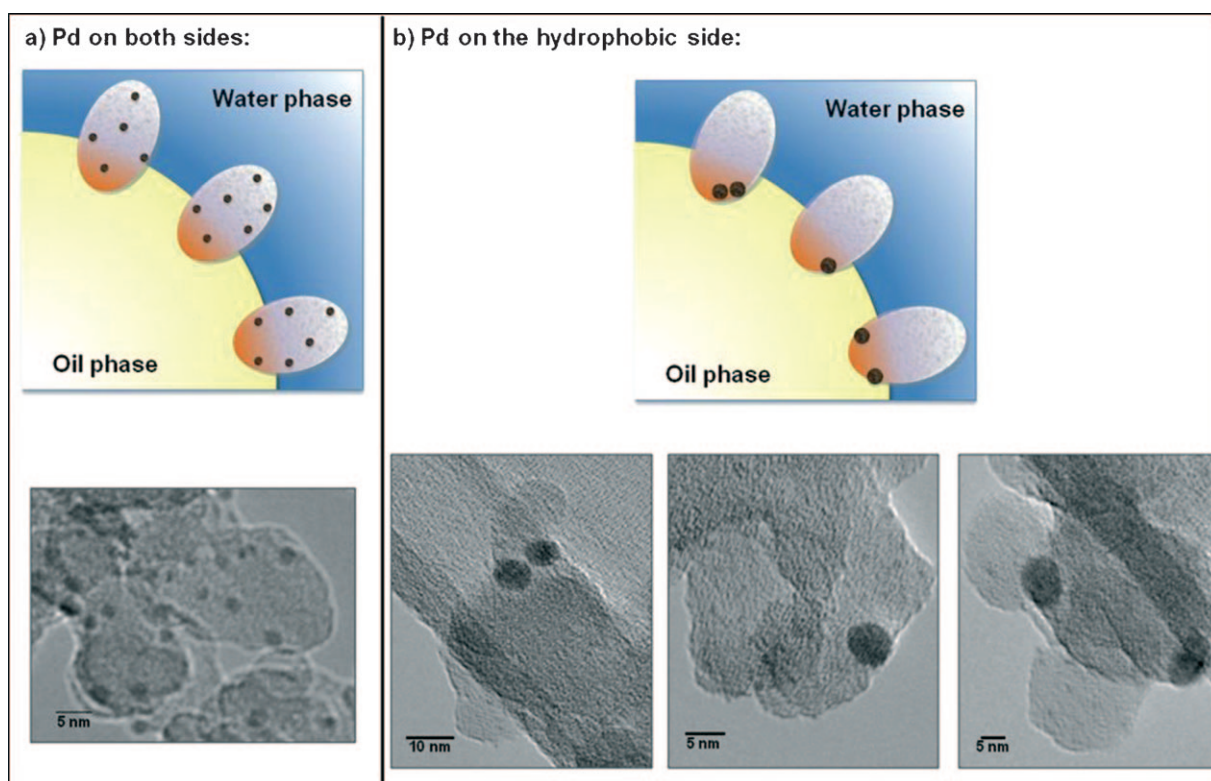
Figure 1. HRTEM images of the Pd/Janus nanoparticles. **a)** Pd deposited on the two sides of the Janus nanoparticles; **b)** Pd selectively deposited on the hydrophobic side.

One can envision many cases in which oil-phase selectivity will be desirable. For example, in biofuel refining it is desirable to combine the dehydration of sugars catalyzed by acid-base catalysts with the metal-catalyzed hydrogenation of the dehydrated product. If the hydrogenation catalyst used in a biphasic system has no preferential orientation at the interface, the dehydration of the sugar will compete with hydrogenation, resulting in a decreased yield. By contrast, in this work a phase-selective hydrogenation catalyst has been placed on the hydrophobic side and consequently, only the molecules stable in the organic phase can undergo hydrogenation. For comparison, we have tested two types of Janus particles. In one of them, the catalytic species are selectively anchored on the hydrophobic side while in the other they are deposited on both sides of the particle.

The synthesized Janus nanoparticles exhibited remarkable ability to stabilize oil-in-water emulsions using decalin as the organic phase. They produced similar or higher fractions of emulsion (up to 90%) and smaller droplet sizes (1–7 μm) than those previously obtained with carbon nanotubes/silica nanohybrids.[1,2] The stabilization of droplets of oil in water indicates that the interface is concave towards the oil, which is related to the higher extent of hydrophilic character of the particles.[13,14,19]

Once the Janus particles were synthesized, two different catalysts were prepared by anchoring Pd on them. In the first one, Pd was deposited on the entire surface of the Janus particles, while in the second one, Pd was only deposited on the hydrophobic side.

High-resolution TEM images were obtained to characterize the products of the two different preparations. As shown in Figure 1, the differences are obvious. The first preparation (Figure 1, **a**) had Pd clusters distributed rather uniformly on the entire surface with an average particle size of 2.5 nm. The second preparation (Figure 1, **b**) had a lower density of Pd particles, deposited on one side of each silica particle. In this case, the size of the Pd particles was larger, around 6 nm. The lower density and larger size of Pd clusters in the second preparation can be explained by: (i) a smaller fraction of support surface available for Pd deposition, and (ii) a decreased anchoring ability of the silica support as a result of the functionalization, making sintering of the metal clusters more favorable during calcination.

To investigate the concept of phase selectivity in emulsion systems, two aldehydes with different solubilities were chosen, benzaldehyde (oil-soluble) and glutaraldehyde (water-soluble). The contrasting solubilities allowed us to follow the evolution of the hydrogenation activity for each molecule, simultaneous-
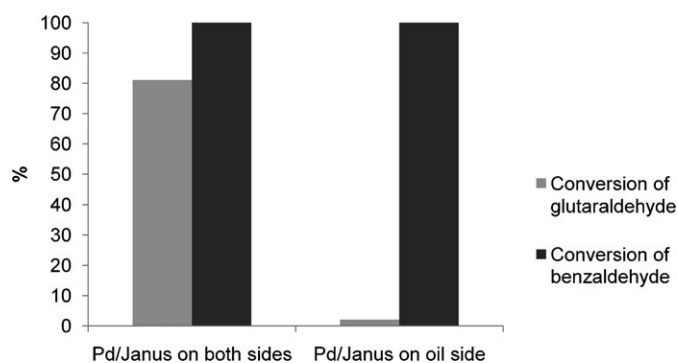
Figure 2. Aldehyde conversion in a semi-batch reactor at 100 °C with a continuous flow of H_2 of 110 sccm through the liquid at a pressure of 1.38 MPa. Amount of catalyst 0.03 g, reaction time 3 h. *Left:* Pd deposited on the two sides of the Janus nanoparticles; *Right:* Pd selectively deposited on the hydrophobic side. The total turnover number (TON) of the hydrogenation of benzaldehyde is 2800 for the catalyst with Pd on both sides and 1488 for the catalyst with Pd on the hydrophobic side. The turnover frequencies (TOF) are 0.99 and 0.49 s^{-1}, respectively.

ly and independently, in the organic and aqueous phases.

The reactants, benzaldehyde and glutaraldehyde, were dissolved in decalin and deionized (DI) water, respectively, before the emulsion was prepared. The concentration was 0.03 M for each aldehyde in each phase. The total volume of the biphasic liquid was 35 mL, keeping an equimolar water/decalin ratio.

Two separate studies were conducted in the emulsion system. In the first run, the Janus catalyst with Pd loaded on both sides of the particles was used to convert the mixture; in the second run, the catalyst

with Pd selectively loaded on the hydrophobic side was used. In each run, 30 mg of catalyst were loaded and the reaction time was 3 h. A detailed description is included in the Supporting Information.

As shown in Figure 2, the differences in behavior were dramatic. When the catalyst contained Pd on both sides of the Janus particles, high conversion levels were obtained for both reactants, about 80% for glutaraldehyde in the water phase and 100% for benzaldehyde in the oil phase. However, when the catalyst had Pd selectively deposited on the hydrophobic side, the conversion of benzaldehyde was kept at 100%, while the conversion of glutaraldehyde decreased to 2%, demonstrating high phase selectivity.

The possible hydrogenation products from each aldehyde are summarized in Scheme 1, along with the simplified reaction network. Benzaldehyde hydrogenation only produces benzyl alcohol. As shown in Table 1, while benzaldehyde only appeared in the organic phase, its product, benzyl alcohol partitioned between the two phases, in a ratio that did not vary with the catalyst used.

On the other hand, as summarized in Table 1, a number of products were obtained from glutaraldehyde. By inspecting the distribution of products between the two phases, an interesting analysis of the reaction/phase migration processes can be made. While glutaraldehyde only appears in the aqueous phase, some of its products distribute between the two phases.

The expected primary product from the hydrogenation of the first carbonyl group, 5-hydroxypentanal, was not observed. By contrast, the cyclic hemiacetal, δ-valerolactol, was observed as a major product, together with the fully hydrogenated 1,5-pentanediol
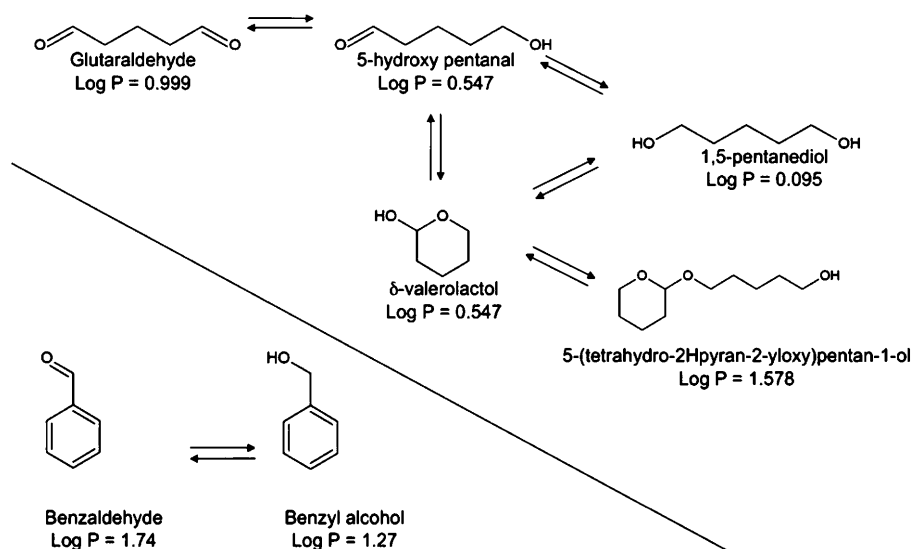
Scheme 1. Reaction network and corresponding products for the hydrogenation of glutaraldehyde (*top*) and benzaldehyde (*bottom*) catalyzed by Pd.

Table 1. Phase composition (before and after reaction). Hydrogenation of aldehydes catalyzed by Pd/Janus nanoparticles at the oil/water interface of the emulsion.

Phase	Compound	Components [mmoles]		
		Before reaction	After reaction	
			Pd on Janus (only oil side)	Pd on Janus (both sides)
Aqueous phase	glutaraldehyde	1.05	1.03	0.20
	δ-valerolactol	0.00	0.02	0.34
	1,5-pentanediol	0.00	0.00	0.51
	5-(tetrahydro-2*H*-pyran-2-yloxy)pentan-1-ol	0.00	0.00	1.60E-03
	benzyl alcohol	0.00	0.55	0.59
	total in aqueous phase	1.05	1.60	1.63
Oil phase	benzaldehyde	1.05	0.00	0.00
	benzyl alcohol	0.00	0.50	0.46
	5-(tetrahydro-2*H*-pyran-2-yloxy)pentan-1-ol	0.00	0.00	3.38E-03
	total in oil phase	1.05	0.50	0.46

when Pd was only on the hydrophillic side. An interesting product that is observed in lower yields is the ether 5-(tetrahydro-2*H*-pyran-2-yloxy)pentan-1-ol. As shown by Van Der Burg et al.,[22] alcohols and aldehydes can form ethers on metal surfaces. In this specific case, it appears that valerolactol and 5-hydroxypentanal form the ether in the aqueous phase; and, after forming, this long ether partitions between the organic and aqueous phases with a higher concentration in the oil.

The network of reactions and transport is schematically illustrated in Figure 3, together with a microscopy image of the type of emulsions stabilized by these Janus catalysts.

To investigate the effect of varying droplet size and interfacial area on the resulting conversion we have conducted two reaction runs by varying the number
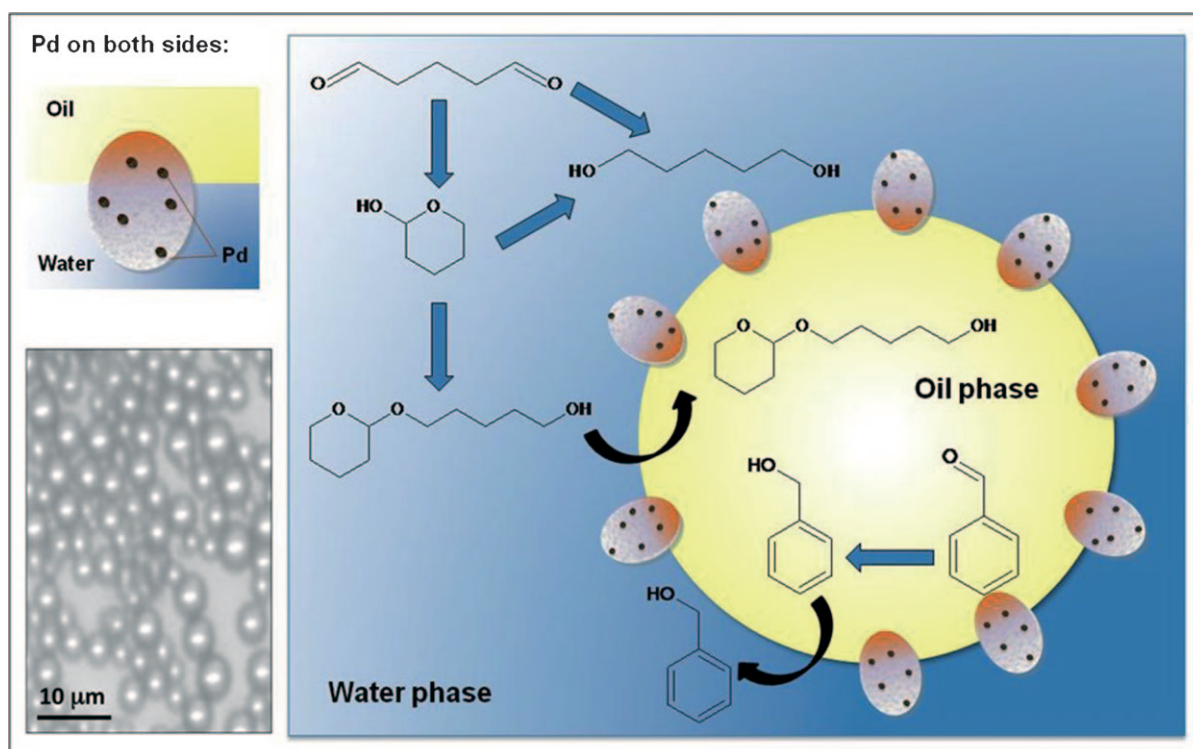
Figure 3. Microscopy image of the oil-in-water emulsion produced with the Janus particles together with an schematic illustration of the hydrogenation reactions taking place at the water/oil interface catalyzed by Pd clusters supported on both sides of the Janus nanoparticles. At the beginning of the reaction, glutaraldehyde is present in the aqueous phase and benzaldehyde in the oil phase.

Table 2. Conversion of benzaldehyde, droplet size and interfacial area in the systems prepared with different particle concentrations.

Catalyst	Droplet size [mm]	Interfacial area [m^2]	Specific interfacial area (m^2 g^{-1} part.)	Conversion of benzaldehyde
5% Pd/Janus oil side	9.4	2.2	73	88%
5% Pd/Janus oil side + Janus (ratio 1:1)	6.4	4.1	68	77%

of Janus particles while keeping constant the amount of catalyst. It has been previously shown[1,13,14,19] that increasing the particle concentration causes a decrease in droplet size and a consequent enhancement in interfacial area. Therefore, in the first run, we used 30 mg of the catalyst of 5% Pd deposited on the hydrophobic side of the Janus particles, and in the second one we mixed 30 mg of this catalyst with 30 mg of pristine Janus particles.

The benzaldehyde conversion obtained in each run, together with the observed droplet size and interfacial area are shown in Table 2.

We observe that, while the interfacial area per mass of nanoparticles slightly decreases in the second run, the total interfacial area increases by almost a factor of two. By contrast, the resulting benzaldehyde conversion does not increase, but rather decreases almost by the same factor as the drop in specific interfacial area. This loss in activity could be due to the aggregation of particles near the interface, which makes the access of the catalytic particles to the interface less effective.

Experimental Section

A detailed description of the synthesis of the Janus silica-nanoparticles and the corresponding Janus catalysts is included in the Supporting Information.

Typical Procedure

Briefly, as shown by Perro et al.[23,24] an emulsion stabilized by silica nanoparticles is first prepared with paraffin wax and water. The silica particles dispersed in a solution of ethanol/water are partially hydrophobized by addition of a surfactant. At 80 °C the wax is melted and after sonication a water/wax emulsion is formed. When cooled down to room temperature, the wax droplets solidify and keep the silica nanoparticles trapped at the wax/water interface. The side of the silica particles free of wax is functionalized with aminopropyltriethoxysilane (APTES), which renders this side of the silica particles hydrophobic. Finally, the wax is dissolved with dichloromethane, releasing the Janus silica-nanoparticles, which are collected by centrifugation.

Two different Janus catalysts were prepared using functionalized silica-nanoparticles as support and Pd clusters as the active species. In the first preparation, Pd was unselectively deposited on the entire surface of the Janus nanoparticles by incipient wetness impregnation of an aqueous solution of Pd(NO$_3$)$_2$ to obtain a metal loading of 5 wt%. In the second preparation, Pd was selectively deposited on the hydrophobic side. The selective deposition was conducted during the initial synthesis of the Janus particles by adding a step, i.e., 5 wt% Pd was incorporated onto the APTES-functionalized Janus particles while they were still embedded in the solidified wax. After vacuum drying, the nanoparticles were collected as described above. Catalysts were dried overnight at 100 °C, calcined in air for 2 h at 200 °C, and stored for subsequent reaction.

Acknowledgements

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