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ARTICLE TYPE

A pH-switched Pickering emulsion catalysis system: high reaction efficiency and facile catalyst recycling

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A smart Pickering emulsion catalysis system is constructed which not only exhibits fivefold reaction rate enhancement effects in comparison to the conventional biphasic system but also can be readily demulsified by tuning pH, allowing for in situ recycling nanocatalysts.

Organic/aqueous biphasic catalysis system is an important platform for many chemical transformations such as hydroformylation, biocatalysis and biomass refining.¹ Despite wide applications, biphasic systems often suffer from low reaction efficiency due to high mass transfer resistance.² To overcome this obstacle, co-solvent, phase-transferable reagents³ and thermoregulated biphasic systems are employed or explored.⁴ These methods, however, require introduction of extra additive or relatively complicated procedures to modify catalysts.

In parallel, recent years have witnessed that nanoparticle catalysts gain unprecedented popularity due to unique properties.⁵ Their practical applications, however, are usually hindered by notorious difficulty in separation and recycling.⁶ Although magnetic-field-assisted separation, ultrafiltration, high-speed centrifugation have been developed to address these issues,⁷ these approaches require external magnetic fields or transferring reaction mixture from the reaction vessel to other vessels. In this context, alternative methods to efficiently recycle nanoparticle catalysts are highly desired.

To address the above two issues our group has recently developed pH-triggered Pickering emulsion (particle-stabilized) inversion system and Pickering emulsion/organic biphasic system.⁸ These systems along with other works exhibit high reaction efficiency due to the large reaction interface area.⁹ However, only a fraction of organic product can be separated at the end of reaction because other fraction is sacrificed in the Pickering emulsion phase. We envision that more organic product would be separated if Pickering emulsion could be broken. However, to detach a nanoparticle from the droplet surface needs to overcome an energy barrier that is several orders of magnitude higher than its thermal energy.¹⁰ To further address this challenge, herein we first demonstrate a smart Pickering emulsion catalysis

system that can be demulsified at the end of reaction. As shown in Figure 1, using appropriate, pH-responsive nanoparticle catalysts (Fig. 1a), one can transfer a conventional biphasic system to water-in-oil (W/O) Pickering emulsion system at the beginning of reaction (Fig. 1b). At the end of reaction, this Pickering emulsion system is demulsified by adding acid and macroscopic phase separation thereby occurs. The organic phase can be isolated through simple liquid transfer whilst the catalyst-contained water can be directly used to the next reaction cycle after tuning the pH.

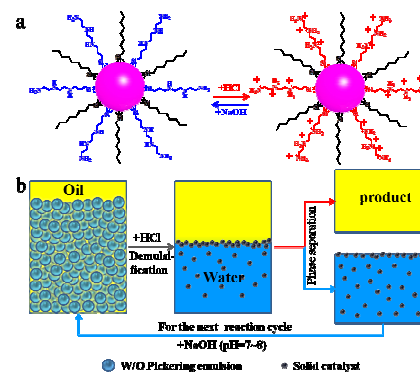


Fig. 1 Schematic illustration of the pH-switched Pickering emulsion strategy. (a) Protonation/deprotonation of a nanoparticle catalyst. (b) Demulsification, organic product separation and catalyst recycling.

The key for this strategy is to obtain smart nanoparticle catalysts that can disassemble at the oil/water interface on command. Thermal and magnetic triggers have reported to break emulsion, yet require high temperature or sufficiently strong magnetic field to overcome high energy barrier.¹¹ In contrast, pH may be a good candidate because it can alter the catalyst surface wettability as so to promote effective demulsification. Although pH-responsive polymer emulsifiers are available in literature,¹² inorganic particles are preferred because of its robustness. As extension to our previous protocol,⁸ we here used a significantly increased molar fraction of pH sensitive $(\text{MeO})_3\text{SiCH}_2\text{CH}_2\text{CH}_2(\text{NHCH}_2\text{CH}_2)_2\text{NH}_2$ (10%, in its mixture with hydrophobic $(\text{MeO})_3\text{Si}(\text{CH}_2)_7\text{CH}_3$) to modify smaller silica nanospheres. The obtained material is denoted as SN-ON. For comparison, we also prepared triamine-monofunctionalized and octyl-monofunctionalized silica microspheres, denoted as SN-N and SN-O, respectively.

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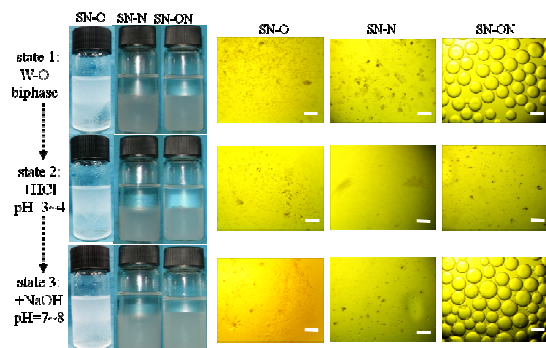


Fig. 2 Appearance of ethyl acetate/water mixture in the presence of different silica nanospheres (photographs taken after standing for 0.5 h). Every vial contains 4 mL ethyl acetate, 4 mL water, and 0.04 g silica nanospheres. State 1: before adding HCl (1 M); State 2: pH is adjusted to 3-4 using HCl; State 3: pH is adjusted to 7-8 using NaOH (1 M). Scale bar is 200 μm .

TEM image shows that SN-ON consists of monodisperse spheres with diameters around 50-60 nm (Fig. S1a, ESI). It is almost non-porous since its specific surface area is only 37 m^2/g (Fig. S2, ESI). The electron energy loss energy (EELS) confirms that triamine and octyl groups are both uniformly distributed on silica nanosphere (Fig. S1b, ESI). The solid state ^{13}C CP-MAS NMR spectrum exhibits C signals, which can be assigned to octyl and triamine groups (Fig. S3a, ESI). In the solid state ^{29}Si CP-MAS NMR spectrum (Fig. S3b, ESI), T^3 [$\text{SiR}(\text{OSi}_3)_3$] and T^2 [$\text{SiR}(\text{OSi}_2(\text{OH}))$] bands appear, indicating that these functionalities are linked to SiO_2 surface through Si-O-Si bonds. Elemental analysis gives quantitative results (Table S1, ESI): octyl and triamine loadings on SN-ON are 0.31 and 0.12 mmol/g, respectively; the octyl loading on SN-O 0.31 mmol/g; triamine loading on SN-N 0.72 mmol/g. These results are broadly supported by the TG result measurement (Fig. S4, ESI).

After mixtures of silica nanospheres, ethyl acetate and water were stirring for 3 min (800 rpm), different phenomena were observed (Fig. 2). For SN-O and SN-N, the systems consist of two phases with SN-O and SN-N distributed in the upper oil phase and the lower water phase, and emulsion droplets were not found with optical microscope. Different from SN-O and SN-N, SN-ON led to a Pickering emulsion phase at the bottom since droplets were observed. The drop test confirmed that it was of W/O type. Interestingly, after adding a few drops of HCl solution, the systems with SN-O and SN-N had no obvious changes, while the SN-ON-stabilized Pickering emulsion was demulsified, as the optical micrographs showed. When a few drops of NaOH solution were added and the pH was tuned to 7-8, the system with SN-ON rapidly restored to Pickering emulsion. Moreover, this reversible switch behaviour was observed in other biphasic systems such as toluene-, benzene-, ether-, dichloromethane- and trichloromethane-water (Fig. S5, ESI). More impressively, the SN-ON-stabilized Pickering emulsion could be reversibly switched on and off at least ten times (Fig. S6, ESI). The significantly different behaviour of these materials is attributed to the difference in surface chemistry. SN-O and SN-N are too hydrophobic or too hydrophilic to stabilize Pickering emulsion, whereas SN-ON is not only moderately hydrophobic but also pH-responsive. After the SN-ON surface triamines are protonated, its surface become too hydrophilic to stabilize emulsion.

Next, hydrogenation was chosen to evaluate the catalysis efficiency and recyclability. We prepared a Pd/SN-ON by loading Pd nanoparticles on SN-ON (Pd loading is 1 wt%). TEM image shows that Pd nanoparticles (1-2 nm in size) are homogeneously distributed on the surface (Fig. S7a, ESI). X-ray (EDX) spectroscopy (EDS) confirms the presence of Pd besides N, C, O and Si elements (Fig. S7b, ESI).

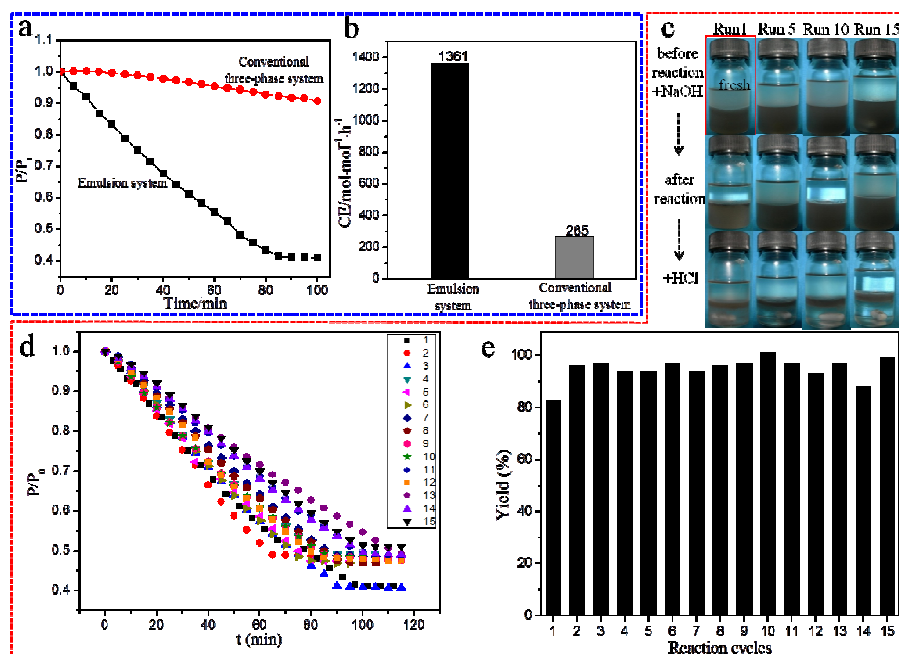


Fig. 3 Results of styrene hydrogenation in the Pickering emulsion and the conventional biphasic. (a) H_2 consumption curves. (b) Catalysis efficiency (CE) (CE = moles of converted substrate / Pd moles \times reaction time h). (c) Photographs for selected reaction cycles. Before reaction, the pH value is adjusted to 7-8 except Run 1; after reaction, the pH value is adjusted to 3-4 to demulsify. (d) H_2 consumption curves for fifteen reaction cycles. (e) Ethylbenzene yields for fifteen reaction cycles. Reaction conditions: 5.6 mL water, 5.6 mL ethyl acetate, 56 mg Pd/SN-ON, 1.1054 g styrene (S/C=2000), 40 $^\circ\text{C}$, 0.35 MPa, 800 rpm. Conventional biphasic system used 1.6 mL isopropyl alcohol and 4 mL water as aqueous phase.

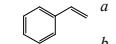
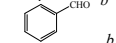
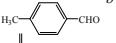
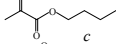
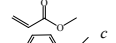
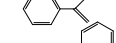
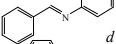
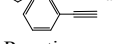
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We compared Pd/SN-ON catalysis efficiency in the Pickering emulsion system and in the conventional biphasic system that was obtained by adding isopropyl alcohol as demulsifier. Based on H₂ consumption rates (Fig. 3a), one can find that these two systems proceeded at remarkably different rates. Fig. 3b quantitatively compares their catalytic efficiency (CE, see footnote of Fig. 3). CE in the Pickering emulsion is 5.14 times higher than that in the conventional biphasic. The significantly enhanced catalysis efficiency is attributed to the presence of emulsion droplets that create large reaction interface area. At the end of reaction, the Pickering emulsion was demulsified after lowering the pH to 3-4, allowing the organic product to separate through a simple liquid decantation (Fig. 3c and Fig. S8, ESI). In the next reaction cycles, Pickering emulsion was obtained again by raising the pH to 7-8. As shown in Figure 3e, ethylbenzene yield is up to 83% in the first reaction, which is higher than those obtained with our previous Pickering emulsion systems.⁸ From the second to fifth cycle, all isolated yields are more than 90%. The slight activity loss is due to the Pd particle aggregation and slight Pd leaching (Fig. S9, ESI)

Table 1 Results of the hydrogenation of various substrates in Pickering emulsion systems.

Substrates	Run 1			Run 2		
	Time /h	Conv. %	Yield %	Time /h	Conv. %	Yield %
	1.5	>99	83	1.2	>99	96
	3	98	81	5	>99	99
	3	>99	78	5	>99	99
	1.5	>99	81	1.5	>99	98
	1.5	>99	82	1.5	>99	98
	1.5	>99	82	1.5	>99	98
	3	>99	82	3	>99	100
	2.5	>99	77	2.5	>99	97

Reaction conditions: ^{a-c} 5.6 mL water, 5.6 mL ethyl acetate, 56 mg Pd/SN-ON and a certain amount of substrate and stirring at 800 rpm. ^a 40 °C, 0.35 MPa, S/C= 2000. ^b 50 °C, 2 MPa, S/C=1000. ^c 40 °C, 2 MPa, S/C=1000. ^d 2 mL water, 2 mL ethyl acetate, 20 mg of Pd/SN-ON, S/C=1000, 800 rpm, 40 °C, H₂ 2 MPa.

This smart system worked well for hydrogenation of other unsaturated compounds. Table 1 lists the results for the first and second reaction cycles. For all the investigated substrates, Pickering emulsion systems gave more than 98% conversions within 1.5-3 h, and 77-82% yields can be achieved with a little amount of product sacrificed at the phase boundary (Fig. S7, ESI). In the second reaction cycle, 99% conversions were afforded and the yields increased up to 97-99%. The results further justify the importance of our smart Pickering emulsion strategy.

In summary, through appropriate surface modification we first demonstrate a pH-responsive Pickering emulsion system for organic/aqueous biphasic catalysis. Such a system exhibits

fivefold reaction rate enhancement effects in comparison to the conventional biphasic reaction. Its demulsification on command not only enables facile separation of organic product but also allows the nanocatalysts to be “in situ” recycled at least 15 times.

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TOC:

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