VIP Emulsion Catalysis

DOI: 10.1002/ange.201300534

A Strategy for Separating and Recycling Solid Catalysts Based on the pH-Triggered Pickering-Emulsion Inversion**

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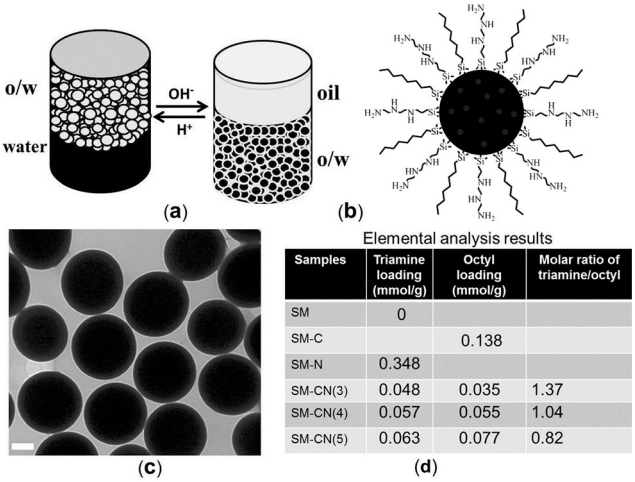
The efficient separation and recycling of catalysts is one of major objectives of sustainable and green chemistry.[1] For liquid-phase reactions, solid catalysts are usually separated from products through filtration or centrifugation. These separation methods are widely used but bothersome, especially when the catalyst particle sizes are in a submicrometer-to-micrometer range, because of catalyst loss, blocking of filters, high time- and energy-consumption, and risk of air oxidation during the course of catalyst transport.[2] These limitations stimulate development of new methods that facilitate catalyst separation and recycling, for example, the currently extensively investigated magnetic-field-assisted separation.[3] We envision if a solid catalyst could be reversibly transferred between two immiscible phases on command, for example, an organic phase and an aqueous phase, the successive catalyst separation and recycling would be facilely conducted in one vessel without need of catalyst transport. Although this idea has been successfully used to separate and recycle homogeneous and polymer-based catalysts in biphasic systems,[4,1i] there are hardly any reports on its implication for separating and recycling heterogeneous (solid particle) catalysts.[2b] The major obstacle is that for micrometer-sized particles, the energy required for crossing the oil/water interface is calculated to be as high as $10^7 K_B T$ (K_B is Boltzmann constant) according to Young's equation, making it thermodynamically impossible.[5]

Submicrometer and micrometer-sized particles with a suitably wettable surface prefer to attach at the oil/water interface, leading to Pickering emulsion [oil-in-water (o/w) or water-in-oil (w/o)].[6] Pickering emulsions are emerging as an attractive platform for designing efficient catalysis systems because they provide a large oil/water reaction interface.[7] More interestingly, if the particle surface is switchable between hydrophilicity and hydrophobicity, Pickering emulsion types can be inverted between o/w and w/o.[8] The emulsion inversion may provide a thermodynamically feasible way of "transferring" solid catalysts because it is not accompanied with detachment of solid particles from the oil/water interface.

Herein, for the first time, we attempt to employ the Pickering-emulsion inversion to address the "phase transfer" of solid catalysts and explore a general concept to successively separate and recycle submicrometer-sized solid catalysts. As shown in Figure 1 a, using an interfacially active and pH-value-responsive solid catalyst, an organic/aqueous biphasic system can be formulated in which an emulsion phase and a neat phase coexist. The protonation and deprotonation make the hydrophilicity/hydrophobicity of the catalyst surface switchable, thus driving emulsion inversion. Before reaction, lowering the pH value of the reaction system leads to an o/w emulsion. Owing to the location of the catalyst particles at the interface of the emulsion droplets, the catalyst can efficiently convert the substrate to product. At the end of reaction, the emulsion is inverted from o/w to w/o after raising the pH value. The solid catalyst is "transferred" into the bottom layer and a neat oil phase is resolved. The resolved organic layer can simply be removed by decantation, and the solid catalyst is "transferred" back into the upper layer after adjusting the pH value for the next reaction cycle. This in situ separation and recycling method may address the limitations of the conventional filtration and centrifugation.



Elemental analysis results

Samples	Triamine loading (mmol/g)	Octyl loading (mmol/g)	Molar ratio of triamine/octyl
SM	0		
SM-C		0.138	
SM-N	0.348		
SM-CN(3)	0.048	0.035	1.37
SM-CN(4)	0.057	0.055	1.04
SM-CN(5)	0.063	0.077	0.82

Figure 1. a) The strategy for catalyst separation and recycling based on the pH-triggered emulsion inversion. b) The structural description for an octyl–triamine bifunctionalized hairy silica microsphere. The gray dots on teh microsphere represent catalytically active centers. c) TEM image of SM-CN(4), scale bar: 100 nm. d) Five types of functional silica microspheres with different loadings of octyl and triamine groups.

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[**] This work was supported by the Natural Science Foundation of China (20903064, 21173137), Program for the Top Young Academic Leaders of Higher Learning Institutions of Shanxi (2011002) and Middle-aged Innovative Talents of Higher Learning Institutions of Shanxi (20120202)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201300534.

We first need to create a material that is interfacially active for producing an emulsion, pH-responsive, and suitable to be used as a catalyst support (although pH-responsive emulsifiers appear in literature,[6a,8a,d] most of them are polymers. For catalysis, inorganic materials are preferred owing to their high stability). We used a mixture of hydrophobic $(MeO)_3Si(CH_2)_7CH_3$ and relatively hydrophilic, pH-sensitive $(MeO)_3SiCH_2CH_2CH_2(NHCH_2CH_2)_2NH_2$ to modify the silica microsphere (SM) by covalent linkage, leading to triamine–octyl bifunctionalized hairy silica microsphere (Figure 1b). To obtain the desired surface chemistry, the molar fraction of triamine silane in the mixture was varied from 3% to 4% and 5% (the total amount of organosilanes was kept constant); the resultant silica microspheres are denoted as SM-CN(x) ($x = 3$–5, respectively). For comparison, we also synthesized octyl-monofunctionalized and triamine-monofunctionalized silica microspheres, denoted SM-C and SM-N, respectively.

SM-CN(x) was characterized with TEM (Figure 1c) and elemental analysis (Table S1 in Supporting Information), X-ray photoelectron spectroscopy (XPS, Figure S1 in Supporting Information), and thermogravimetry (TG, Figure S2 in Supporting Information). SM-CN(x) is spherical in morphology and its diameter is in a range of 250–350 nm (Figure 1c). According to the elemental analysis results, the triamine loading on SM-N is much higher than the octyl loading on SM-C because the alkaline triamine itself has ability to catalyze the surface silylation (Figure 1d). For the bifunctionalized samples, both the triamine and octyl loadings gradually increase from SM-CN(3) to SM-CN(4) and SM-CN(5). Notably, the molar ratio of triamine to octyl gradually decreases, suggesting that the surface chemistry can be influenced by changing the molar fractions of these two organosilane.

We examined the interfacial activity and emulsion-inversion ability of the synthesized samples. After addition of an equal volume of toluene into water containing 0.8 wt% of the sample (with respect to water), and subsequent shaking (800 rpm for 3 min) or vigorous stirring (3000 rpm for 5 min), different phenomena were observed for these samples (Figure 2). Bare silica microsphere (SM) precipitated at the bottom, while SM-N was mainly dispersed in water layer. SM-C, SM-CN(3), SM-CN(4), and SM-CN(5) were well distributed in the bottom layer with good stability against sedimentation (at least two weeks). Optical microscopy confirmed that the bottom layer was a Pickering emulsion phase because spherical droplets were clearly observed (microscopic images for SM-CN(4) in Figure 3a, microscopic images for other samples in Figure S3 in Supporting Information). Interestingly, after adding a few drops of aqueous HCl solution and stirring, only SM-CN(3) and SM-CN(4) transferred to the upper layer where Pickering emulsion was also observed (Figure 2, Figure 3b SM-CN(4) has a better emulsifying efficiency than SM-CN(3), judging from the emulsion phase height). More interestingly, SM-CN(3) and SM-CN(4) again rapidly transferred back to the bottom layer after a few drops of NaOH solution were added (Figure 2), where emulsion droplets were still observed (Figure 3c).

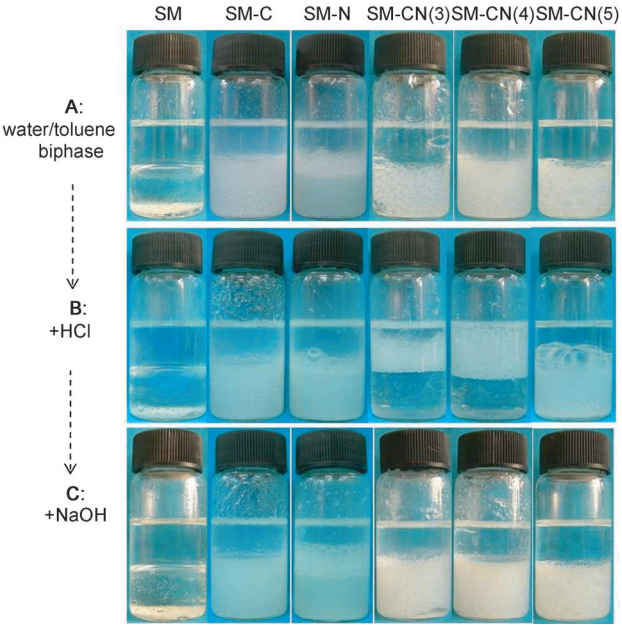

Figure 2. The appearance of toluene/water systems in the presence of various silica microspheres (all photographs were taken after the samples had being stabilized for 0.5 h). A) the biphasic system contains 4 mL of toluene, 4 mL of water, and 0.032 g of silica microsphere or functionalized silica microsphere; B) adding a few drops of HCl (1 mol L^{-1}) to (A) the pH value is adjusted to 3–4; C) adding a few drops of NaOH (1 mol L^{-1}) to (B) and the pH value is re-adjusted to 7–8.

The differences in the emulsion-inversion ability are related to the pH-responsive surface chemistry. As shown in Figure 3d (zeta potentials), under the neutral conditions (pH 6.8), the zeta potential SM-CN(4) was measured to be approximately 0. Under the acidic conditions (pH 3.1), it was +30.1 mV, indicating the protonation of the surface triamine. As the pH value increased, the zeta potential gradually decreased owing to the deprotonation of protonated triamines. When the pH value reached 7.9, the zeta potential became slightly negative (−3.1 mV), suggesting a nearly full deprotonation of the protonated triamines. The triamine protonation at the low pH values makes the SM-CN(4) surface hydrophilic owing to it bearing charges, whereas the deprotonation of protonated triamines at the high pH values renders the SM-CN(4) surface hydrophobic. This pH-triggered hydrophilicity/hydrophobicity switching was confirmed by water contact angle measurements (Figure 3d). The water contact angle of fresh SM-CN(4) was 110° (Figure 3d point a), whereas the water contact angle of SM-CN(4) treated with an acidic aqueous solution (pH 3.9) decreased down to 61° (point b). When the protonated SM-CN(4) was further treated with a basic solution (pH 7.9) its water contact angle restore the value (109°, point c). As expected, such changes drive the SM-CN(4)- and SM-CN(3)-stabilized emulsion inversion between o/w and w/o (the emulsion types were verified by the conductivity measurement and emulsion droplet test).[8] The hydrophobicity/hydrophilicity of SM and SM-C is almost unchangeable because of the absence of a pH-sensitive moiety. SM-N is relatively hydro-

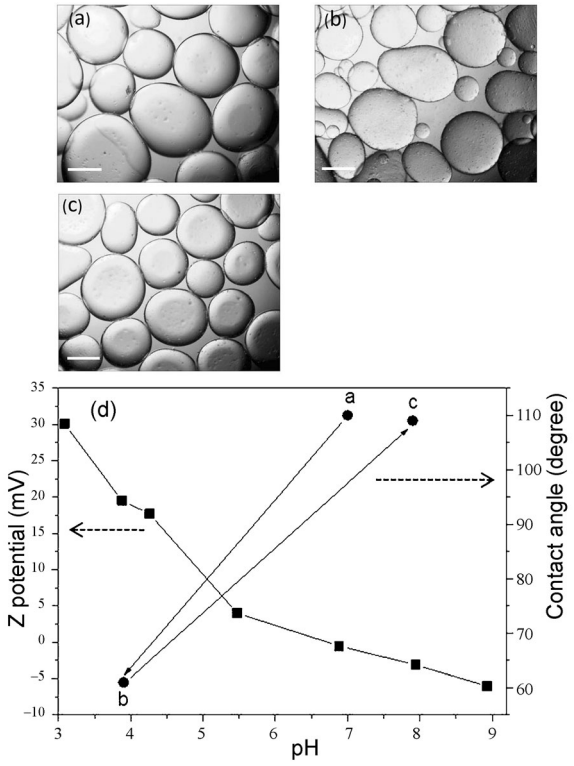

Figure 3. Microscopic image, zeta potentials, and water contact angles of SM-CN(4). a) Microscopic image of the SM-CN(4)-stabilized emulsion, neutral pH, scale bar: 200 μm. b) Microscopic image of the SM-CN(4)-stabilized emulsion, pH 3–4, scale bar: 200 μm. c) Microscopic images for the SM-CN(4)-stabilized emulsion, pH 7–8, scale bar: 200 μm. d) Zeta potentials of SM-CN(4) at different pH values and water contact angles of SM-CN(4) treated with different pH value water, see text for details.

philic and its surface is more hydrophilic after protonation. The low molar ratio of triamine/octyl makes SM-CN(5) relatively hydrophobic, and the protonation does not makes its surface sufficiently hydrophilic. The hydrophobicity/hydrophilicity of SM-N and SM-CN(5) is changeable but not in an appropriate range (The contact angles switchable in the vicinity of 90° is likely to invert emulsion).[8f,9]

In addition to the toluene/water system, SM-CN(4) is a good emulsifier for using ethyl acetate, benzene, ether, dichloromethane, and trichloromethane as the oil phase (Figure S4–9 in Supporting Information). In these systems, all Pickering emulsions can be inverted easily between o/w and w/o through regulation of the pH value (changing temperature was found to be ineffective for inversion of our emulsion system). The process was accomplished within less than six minutes under stirring. Most importantly, the inversion was highly reversible in a wide range of oils. After 10 cycles the Pickering emulsion was still formed and the neat organic phase could be well resolved (Figure S4–9). Additionally, the emulsion inversion was observed in the presence of different fractions of SM-CN(4) (Figure S10 in Supporting Information).

For the above formulated 1:1 (v/v) biphasic systems where an emulsion phase and a neat phase coexist, we estimated the oil volume fraction in the emulsion phase at pH 3–4, and the resolved oil volumes at pH 7–8. These results are given in Table S2 in Supporting Information. In the o/w emulsions (at pH 3–4), the oil volume fractions in the emulsion phase are in the range of 83.0–91.7% for these six solvents. The high internal oil phase is helpful for the sufficient contact between catalyst and reactants. At pH 7–8, 68.8–83.8% of the initial oil can be resolved after emulsion inversion. The high fraction of the resolved oil aids the separation of more products from the catalyst-containing emulsion phase. Moreover, after removing the resolved oil layer, the remnant emulsion still exhibits good stability without any coalescence (Figure S11 in Supporting Information, 24 h), which allows for a sufficient time flexibility to transfer the upper products.

These investigations establish that the SM-CN(4)-stabilized emulsion system tolerates a variety of oils, has a high internal oil phase, flexible formulation, rapid inversion, and good ability to resolve oil. Such properties are favorable to design efficient and recyclable catalysis systems. As a proof of the concept, we prepared a solid catalyst Pd/SM-CN(4) by depositing Pd nanoparticles onto SM-CN(4) and tested them. (The TEM images of Pd/SM-CN(4) are in Figure S12a–c in the Supporting Information. The Pd loading is 0.46 wt% and its particle sizes are in the range of 2–4 nm. XPS investigations confirm that Pd^{II} was fully reduced to metallic Pd^0 in Figure S12d. The N_2 sorption isotherm is reflected in Figure S12e.)

The hydrogenation of olefin (styrene) in the organic/aqueous biphasic system was used as a model reaction to evaluate the catalysis efficiency and the ability of separating and recycling catalyst (reaction conditions: 0.1 mol% Pd with respect to substrate, ambient pressure of H_2, room temperature, and 1200 rpm). Before reaction, the water pH value was adjusted to 3–4. The Pd/SM-CN(4)-stabilized emulsion (the droplets are 100–400 μm in size and the viscosity is 11.3 MPa s at a shear rate of 300 s^{-1}) was formed in the upper layer (o/w) after shaking or vigorous stirring. At the end of reaction, the solid catalyst Pd/SM-CN(4) was still in the upper layer (Figure S13 in Supporting Information). To separate the product from the catalyst, a few drops of NaOH solution was added and the pH value re-adjusted to 7–8. Pd/SM-CN(4) was observed to transfer into the lower layer within several minutes. The o/w emulsion changed to the w/o emulsion and the extra oil was quickly resolved. The resolved upper organic layer could be transferred through a simple decantation. The conversion of styrene was more than 99% within 1.5 h (the first bar in Figure 4. This reaction efficiency is slightly lower than that for using pure ethyl acetate as solvent (99% conversion, 1 h). We further evaluated the catalytic efficiency of this emulsion system through a comparison with three other biphasic systems that are schematically described in Figure 4 (their actual reaction states are reflected in Figure S13 in Supporting Information). Interestingly, the conversion obtained with the Pd/SM-CN(4)-stabilized o/w emulsion system was much higher than that of the system without emulsification (the second histogram, 52% conversion. At the end of the reaction, some of the solid catalyst was found at the two phase boundary where a small amount of droplets was formed due to stirring). Moreover, it is much higher than that

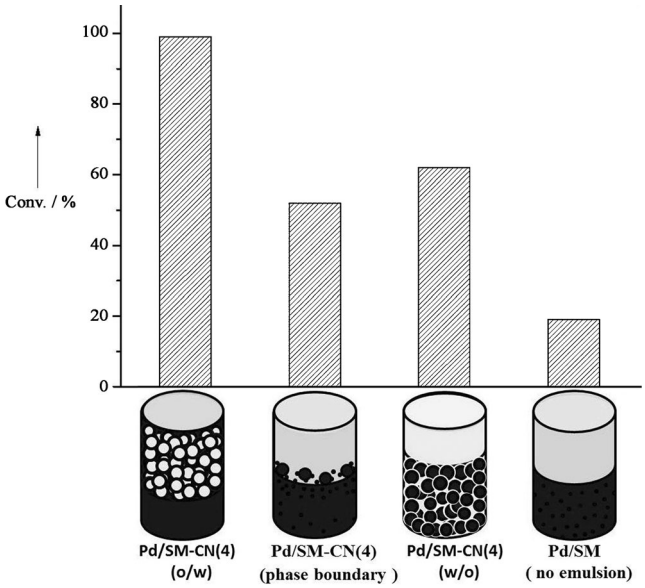

Figure 4. The results of the styrene hydrogenations in different biphasic systems. Pd/SM-CN(4) (o/w): using Pd/SM-CN(4) as catalyst, o/w emulsion was formed at pH 3–4 after emulsification. Pd/SM-CN(4) (phase boundary): using Pd/SM-CN(4) as catalyst (pH 3–4, without emulsification), some of the solid catalysts was found at the biphasic boundary. Pd/SM-CN(4) (w/o): using Pd/SM-CN(4) as catalyst, w/o emulsion was formed after emulsification, without addition of acid and base (pH 7). Pd/SM (no emulsion): using Pd/SM as catalyst (unmodified silica sphere as support), an emulsion was not found in this reaction system. The actual catalyst distributions in the biphasic systems are shown in Figure S13 in Supporting Information.

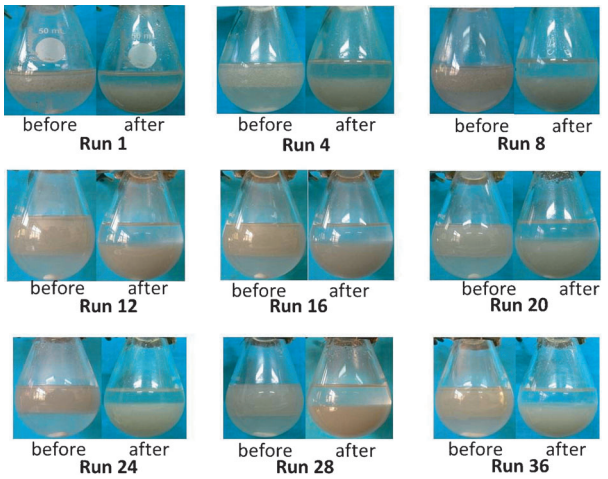

Figure 5. Photographs of the pH-triggered catalyst separation and recycling based on the emulsion inversion. Before: at the beginning of reaction (the pH value is adjusted to 3–4). After: at the end of reaction (the pH value is adjusted to 7–8).

of the Pd/SM-CN(4)-stabilized w/o emulsion system (the third bar in Figure 4, 62% conversion. This is also confirmed by other types of reactions (Figure S14 in Supporting Information), five-times higher than those of the Pd/SM-catalyzed biphasic system (the last bar in Figure 4, at pH 3–4, no emulsion, 19% conversion). The comparison of these results clearly indicates that the Pd/SM-CN(4)-stabilized o/w emulsion system has a much higher catalytic efficiency than the other biphasic systems. The reaction efficiency difference of the emulsion systems mainly originates from mass transfer effects (Table S3 in Supporting Information).

The conversions of various olefins reach 90–99% within 5 h (Table S4 in Supporting Information), indicating the good efficiency of the emulsion system. Moderate yields were achieved in the first reaction cycles because a part of product was sacrificed in the lower emulsion layer. To recycle the catalyst, the fresh substrate was added and the pH value was re-adjusted to 3–4. The solid catalyst quickly came back into the upper layer. All the second reaction cycles still proceeded efficiently without decrease in activity (Table S4 in Supporting Information). Note that the "yields" for the second reaction cycles increased by up to 80–102% because the continuous phase of emulsion was already supplied in the first reaction cycles. Moreover, the emulsion catalysis could be extended to other systems such as toluene/, ether/, and benzene/water systems (Table S5 in Supporting Information).

Quite impressively, the emulsion catalysis system is highly recyclable, which is highlighted by 36 reaction cycles (Figure S15). The selected photographs for the reaction cycles are displayed in Figure 5. Throughout the 36 reaction cycles, the product–catalyst separation and catalyst recycling were conducted facilely by only adjusting the pH values, thus circumventing the aforementioned limitations of conventional separation methods. The yields are presented in Figure 6.

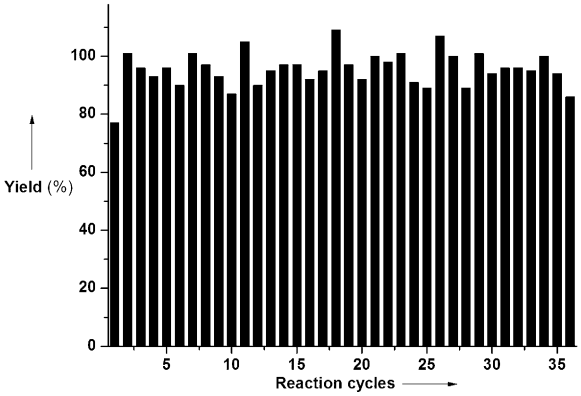

Figure 6. The recycling results of the Pd/SM-CN(4)-catalyzed hydrogenation of styrene in the ethyl acetate/water system (0.5–2 h. The reaction conditions are included in the Supporting Information).

Although the ethylbenzene yield was moderate (77%) in the first reaction cycle, 86–108% "yields" could be obtained from the second to the thirty-sixth reaction cycles (the variation of yields is mainly due to the effects caused by the produced NaCl and the different phase separation time for each reaction cycle; "yields" over 100% are because the partial product comes from the previous reaction cycle). The high yields and excellent recyclability are indications of the high effectiveness of our strategy. To our knowledge, it is one of the best results among various methods for catalyst recycling.

To further justify the high effectiveness of this method, we determined the residual Pd in the resolved organic layer with ICP-AES. In the first reaction cycle, the residual Pd concentration was determined as 0.1 ppm. In the sixteenth and thirty-sixth cycles, the residual Pd concentrations were below 0.1 ppm. After 36 reaction cycles, spherical emulsion droplets were still observed (Figure S16 in Supporting Information). The recyclability is attributed to the strong adsorption of the solid catalyst at the oil/water interface. This adsorption means that the energy obstacle for detachment from the interface is so high that the catalyst cannot leach into the resolved oil phase.[5] Moreover, SM-CN(4) was generalized to load other metals such as Rh. The resultant Rh/SM-CN(4) catalyst also showed high activity, and could be recycled by the pH-triggered strategy (Figure S17 in Supporting Information).

In summary, by tailoring the surface chemistry by using combined organosilanes, we have prepared interfacially active silica microspheres for the formation of Pickering emulsions. With this multifunctional silica as a catalyst support, the formulated catalyst-stabilized emulsion system shows much higher efficiency than its analogous biphasic systems. More importantly, based on Pickering-emulsion inversion, we have successfully developed a conceptually novel method for in situ separate and recycling of submicrometer-sized solid catalysts by tuning the pH value. This method is time/energy saving for the catalyst separation and recycling. Its high effectiveness is highlighted by 36 reaction cycles and negligible catalyst loss. The overall efficiency of a chemical process may be significantly improved and the work-up method may be simplified because the successive catalyst separation and recycling can be processed in one reaction vessel. The pH-triggering for separation and recycling of solid catalysts can probably be extended to thermo-triggering,[8] making our method more generally accessible to sustainable and green catalysis.

Experimental Section

Preparation of SiO_2-CN(x): 1.0 g of SiO_2 microsphere (dried at 125 °C for 4 h) was dispersed into toluene (5 mL). The required amount of $(MeO)_3SiCH_2CH_2CH_2(NHCH_2CH_2)_2NH_2$ and $(MeO)_3Si(CH_2)_7CH_3$ were simultaneously added. After heating under reflux at 110 °C for 4 h under N_2 atmosphere, the material obtained was isolated by centrifugation, washed five times with toluene and dried. The total amount of organosilanes was kept at 1.5 mmol. The molar fraction of triamine silane in the total silylating reagents was changed from 3% to 4% and 5%. The modified silica microspheres are accordingly denoted as SM-CN(x), where $x = 3$, 4, and 5.

Received: January 21, 2013
Revised: April 1, 2013
Published online: June 7, 2013

Keywords: biphasic reactions · catalyst separation · heterogeneous catalysis · Pickering emulsions

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