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Tuning Biphasic Catalysis Reaction with a Pickering Emulsion Strategy Exemplified by Selective Hydrogenation of Benzene

Yabin Zhang,[a] Ming Zhang,[a] and Hengquan Yang*[a]

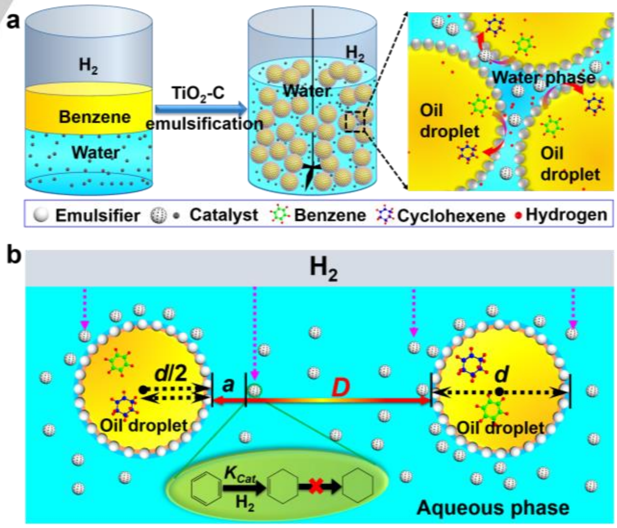
Abstract: Although organic/aqueous biphasic catalysis reactions are widely used, it is difficult to effectively control their reaction process. Here we develop a solid particles-stabilized emulsion (Pickering emulsion) strategy to address this limitation. A challenging biphasic reaction, selective hydrogenation of benzene to cyclohexene, was investigated as a case. The developed Pickering emulsion system exhibited higher catalysis efficiency and selectivity than the conventional biphasic reaction system even under mild stirring. The cyclohexene selectivity and yield in the Pickering emulsion system reached as high as 51.2% and 43.3%, respectively. More importantly, the findings presented here demonstrate the feasibility that the reaction rate and selectivity of challenging biphasic reactions can be regulated by the rational adjustment of Pickering emulsion parameters including emulsion droplet size, droplet distance as well as emulsion type, which is otherwise unattainable for conventional biphasic reaction systems.

Introduction

Organic/aqueous biphasic catalytic system is an important platform for many chemical transformations such as synthesis of fine chemicals, biocatalysis and biomass refining.[1] Despite extensive applications, biphasic systems often suffer from low reaction efficiency due to their high mass transfer resistance.[2] To improve their mass transfer rate, vigorous mechanical agitation has to be employed.[3] By doing so, one of the liquids is homogenized into liquid droplets, which are dispersed in the other liquid under incessant high-speed agitation.[4] However, the liquid droplets generated by mechanical agitation are often large in size, and at the same time the droplets are very unstable and prone to coalescence, driven by the high interfacial tension.[5] For example, despite of the agitation speed, the average droplet sizes no longer decreased after they were downsized to *ca.* 270 μm.[6] Moreover, the droplet size, the average distance between droplets and the homogeneity of the biphasic reaction systems are still difficult to control precisely through mechanical agitation.[7] Consequently, the reaction outcomes such as conversion, selectivity and yield are unlikely to control at a desired level. This is especially true for those multistep biphasic reactions, of which the conversion, selectivity and yield are sensitive to the mass transport.[8] In this context, it is urgent to explore new efficient methods that enable the biphasic catalysis reaction to take place at a controllable level.

Pickering emulsions that are stabilized by solid particles are emerging as an innovative platform for designing efficient biphasic catalysis systems.[9] In comparison to conventional surfactant-stabilized emulsions, Pickering emulsions are more stable against coalescence even at high temperatures due to the high adsorption energy of particles at oil/water interfaces.[10] Moreover, Pickering emulsions allow their droplet sizes to tune.[11] For example, our group had prepared Pickering emulsions with droplet sizes ranging from 40 to 1000 μm, realizing careful investigation of the relationship between catalytic efficiency and droplet size.[12] Besides their tunable droplet sizes, it is conceivable that in the Pickering emulsion systems the average distance between two adjacent droplets can be tuned since the droplets have high stability. This is also crucial for those multistep biphasic catalysis reactions aforementioned. These merits and envisioning prompt us to use Pickering emulsion systems to address the limitations associated with challenging biphasic catalysis reactions.

Selective hydrogenation of benzene to cyclohexene has been proven as an important route for producing cyclohexene, an important intermediate chemical for producing cyclohexanol, caprolactam and adipic acid.[13] Compared to other routes, this method has many advantages such as inexpensive feedstock, atomic economy and energy saving.[14] However, the selective



Scheme 1. (a) Schematic description of an O/W Pickering emulsion strategy for selective hydrogenation of benzene; (b) microscopic presentation for mass transfer during the selective hydrogenation of benzene in the O/W Pickering emulsion reaction system. *d* is the droplet diameter; *a* is the average distance between the droplet interface and the catalyst particle; *D* is the distance between droplets.

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hydrogenation of benzene to cyclohexene is thermodynamically unfavorable since its Gibbs free energy change is −23 kJ mol^{-1}, which is much higher than that for the complete hydrogenation of benzene to cyclohexane (−98 kJ mol^{-1}).[15] Over past twenty years, it has been demonstrated that this challenging limitation can be overcome by exploiting the kinetics of organic/aqueous biphasic reaction.[16] The selectivity toward cyclohexene in the biphasic system can be improved significantly. The reason is that water can promote rapid departure of cyclohexene from water to organic phase due to its low solubility in water, thereby avoiding further hydrogenation to cyclohexane.[17] We envision that if the key parameters of the biphasic selective hydrogenation of benzene such as the droplet size and the droplet distances can be tuned, the cyclohexene selectivity and yield would be improved further.

Herein, we use Pickering emulsion strategy to perform the biphasic reaction at a controllable level, which is for the first time exemplified by selective hydrogenation of benzene to cyclohexene, as shown in Scheme 1a. The impacts of the emulsion type, droplet size and the average distance between two adjacent droplets on the cyclohexene selectivity and yield were investigated in detail. The cyclohexene yield in the O/W Pickering emulsion system was shown to have a significant increase in comparison to its conventional biphasic counterpart system. The results presented here well demonstrate that the selectivity and yield of multistep biphasic catalysis reactions can be tuned through regulating Pickering emulsion droplet size, distance between droplets as well as Pickering emulsion types.

Results and Discussion

Preparation and characterization of interface-active particles.

In order to transform a conventional benzene/water biphasic system to a Pickering emulsion system, we first need to prepare particles with proper wettability, which are used as emulsifiers to stabilize an O/W or W/O Pickering emulsion. Commercially available TiO_2 nanoparticles (NPs) are a widely used catalyst support due to the high stability and low-cost.[18] However, the commercial TiO_2 nanoparticles are too hydrophilic to stabilize Pickering emulsions. To render them hydrophobicity, we used two doses of $(MeO)_3SiCH_3$ to modify the surface of TiO_2: 0.4 mmol/g and 4 mmol/g (with respect to TiO_2). The latter modified TiO_2 was expected to be more hydrophobic than the former because of high loading of methyl group. The morphology of TiO_2 NPs and the modified TiO_2 NPs was observed with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figure 1, TiO_2 NPs show approximately a cubic morphology with a mean diameter of 21 nm although they are somewhat aggregated. After modification, TiO_2 NPs still retain their original morphology without severe aggregation. The modified TiO_2 was characterized with FT-IR spectroscopy. From the FT-IR spectrum in Figure 2a, peaks at 2850−2950 cm^{-1} and 1485 cm^{-1}, corresponding to C-H stretching vibrations and C−H scissoring vibrations, are clearly observed. This is an indication that methyl groups were successfully grafted on the surface of TiO_2 NPs. The intensity of these two characteristic peaks of TiO_2-C(4) is higher than that of TiO_2-C(0.4), which accords with the experimental dose. TG measurement was performed to further examine the loading of methyl group and the thermal stability of the emulsifiers. As shown in Figure 2b, TG curves exhibit that three stages of weight loss. The first stage was observed in the range of 50−150 ^{o}C, which was associated to the loss of physically adsorbed water. The second stage of weight loss occurred in the range of 150−400 ^{o}C, which was mainly related to the decomposition of methyl groups. The third stage from 400 to 700 ^{o}C was mainly caused by the condensation dehydration of hydroxyl groups. According to the TG results, the methyl loadings are estimated to be about 0.22 mmol/g (1.13% weight loss) for TiO_2-C(0.4) and 0.33 mmol/g (1.99% weight loss) for TiO_2-C(4), respectively. These loadings are broadly consistent with the results determined by elemental analysis (Figure 2c). To examine the surface wettability of the modified TiO_2 NPs, we measured their water contact angles. As shown in Figure 2d, the water contact angle for the unmodified TiO_2 is only 30.3^{o}. The contact angle for TiO_2-C(0.4) increases to 89.2^{o}, confirming its partially hydrophobic. In contrast, the contact angle for TiO_2-C(4) reaches

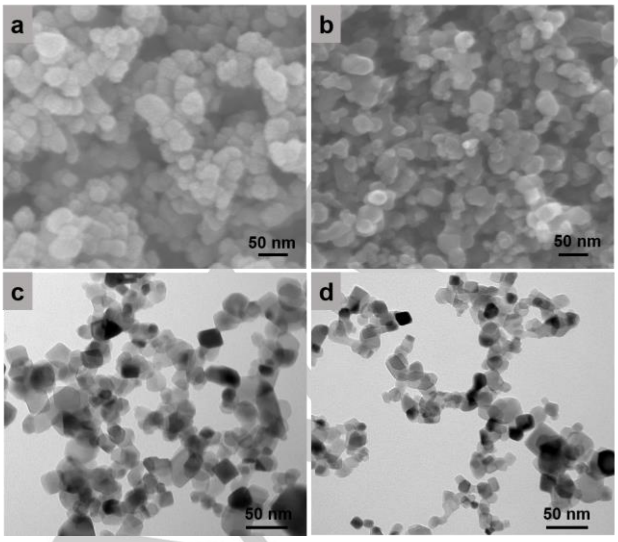

Figure 1. (a) SEM image of unmodified TiO_2; (b) SEM image of methyl-modified TiO_2 with a methyl loading of 0.4 mmol g^{-1}; (c) TEM image of unmodified TiO_2; (d) TEM image of methyl-modified TiO_2 with a methyl loading of 0.4 mmol g^{-1}.

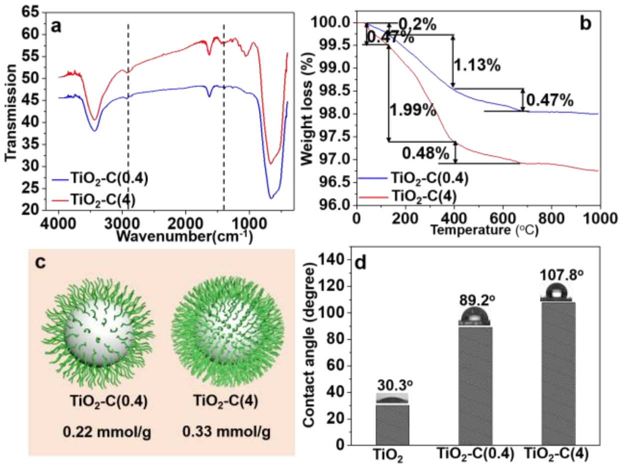

Figure 2. (a) FT-IR spectra of TiO_2-C(0.4) and TiO_2-C(4); (b) TGA curves of TiO_2-C(0.4) and TiO_2-C(4); (c) results of elemental analysis of TiO_2-C(0.4) and TiO_2-C(4); (d) water contact angles of the unmodified TiO_2, TiO_2-C(0.4) and TiO_2-C(4).

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as high as 107.8°, being hydrophobic. Such a change in the surface wettability is also in agreement with the changes in the loading of hydrophobic methyl group.

Preparing Pickering emulsions for selective hydrogenation of benzene

A Ru/TiO_2 catalyst for the selective hydrogenation of benzene was prepared by loading Ru nanoparticles on the above unmodified TiO_2 via an impregnation-reduction process.[19] The TEM images in Figure S1 clearly show that Ru nanoparticles are uniformly dispersed on the surface of TiO_2. Their average size is estimated to be about 3.3 nm. The water contact angle of the Ru/TiO_2 catalyst was measured to be 33.5°, suggesting its surface is highly hydrophilic (Figure S2). After vigorously stirring a mixture of benzene, water containing $ZnSO_4{\cdot}7H_2O$ (3 g, as inorganic additive)[19] and the Ru/TiO_2 catalyst (0.15 g) in the presence or absence of the emulsifier TiO_2-C(0.4) or TiO_2-C(4), different phenomena were observed. For the case of the absence of the emulsifier TiO_2-C(0.4) or TiO_2-C(4), this system is still a conventional biphasic suspension since no droplets were observed with optical microscopy (Figure S3). The Ru/TiO_2 catalyst particles were distinctly dispersed in the bottom layer (water phase), due to their high hydrophilicity. In the case of the presence of the emulsifier TiO_2-C(0.4), droplets with mean size of 60 μm appeared (Figure 3a). This emulsion is confirmed to be an oil-in-water Pickering emulsion because the fluorescence microscopy reveals the distribution of the oil-soluble Nile red in oil (benzene) droplet (Figure 3c). Different from the case of TiO_2-C(0.4), the TiO_2-C(4)-stabilized Pickering emulsion belongs to a water-in-oil type with droplets size of 56 μm (Figure 3b), which is also supported by fluorescence microscopy image, in which water-soluble FITC-dextran is distributed within the droplets (Figure 3d). The dependence of emulsion type on the emulsifier agrees with the general principle that partially hydrophobic particles tend to stabilize oil-in-water Pickering emulsions, while hydrophobic particles is favorable to stabilize water-in-oil Pickering emulsions.

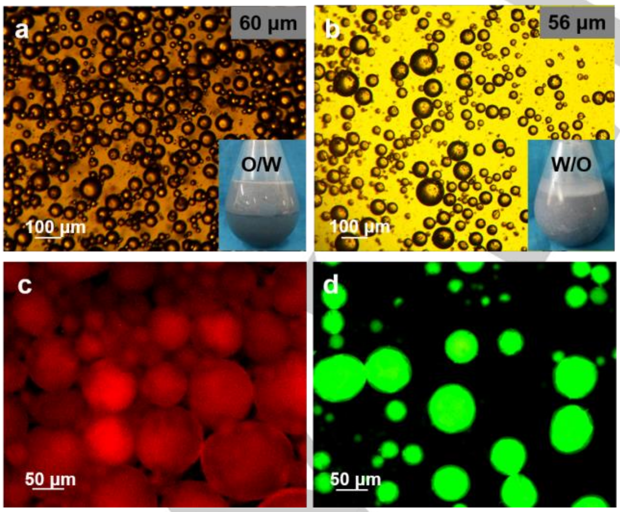

Figure 3. (a) Optical microscopy image of the O/W Pickering emulsions stabilized by TiO_2-C(0.4), inset showing its appearance; (b) optical microscopy image of the W/O Pickering emulsion stabilized by TiO_2-C(4), inset showing its appearance; (c) fluorescence confocal microscopy image of the O/W Pickering emulsion with the oil phase dyed by oil-soluble Nile Red; (d) fluorescence confocal microscopy image of the W/O Pickering emulsion with the water phase dyed by water-soluble FITC-dextran. The Pickering emulsion comprises of 0.15 g catalyst, 15 mL benzene, 30 mL H_2O, 3 g $ZnSO_4{\cdot}7H_2O$ and 1 wt% emulsifier (with respect to dispersed phase).

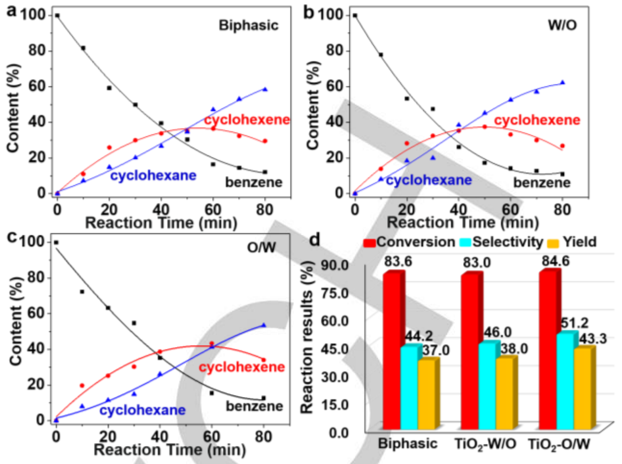

Figure 4. (a) Kinetic profiles of the selective hydrogenation of benzene over Ru/TiO_2 in a conventional biphasic system; (b) kinetic profiles of the selective hydrogenation of benzene over Ru/TiO_2 in the W/O Pickering emulsion system; (c) kinetic profiles of the selective hydrogenation of benzene over Ru/TiO_2 in the O/W Pickering emulsion system; (d) reaction results obtained at the maximum yield of cyclohexene, calculated based on the reaction within the first 60 min for the conventional biphasic system and the O/W Pickering emulsion system, the first 50 min for the W/O Pickering emulsion system. Reaction conditions: 0.15 g catalyst, 15 mL benzene, 30 mL H_2O, 3 g $ZnSO_4{\cdot}7H_2O$, 5.0 MPa H_2, 140 °C, 1000 rpm for the conventional biphasic reaction system and 700 rpm for the Pickering emulsion reactions, 1wt% emulsifier (with respect to the dispersed phase) for Pickering emulsion systems.

Impact of reaction system

Next, we investigated the selective hydrogenation of benzene in the above three systems. The reactions were conducted at 140 °C under 5 MPa H_2. Their reaction kinetics were monitored with GC, as shown in Figure 4a-c. In these three systems, with time the benzene concentration gradually decreased, the cyclohexane concentration increased, and the cyclohexene concentration first increased and then shrunk. This tendency indicates that cyclohexene is the intermediate product of this two-step reaction, which can be further hydrogenated to cyclohexane. However, these three systems differ in reaction rate. For the conventional biphasic system, high-speed agitation (at 1000 rpm) had to be implemented to obtain a satisfactory reaction efficiency. Cyclohexene in 37% yield at the benzene conversion of 83.6% was given within 60 min (Figure 4d). For the Pickering emulsions, we found it unnecessary to employ such a high-speed agitation since they already have sufficiently high reaction interface areas. Accordingly, a rate of 700 rpm was implemented. In the W/O Pickering emulsion system, the maximum yield of cyclohexene was 38% at the benzene conversion of 83% within 50 min (Figure 4d). Although the W/O Pickering emulsion system is almost equal to the conventional biphasic system in terms of the selectivity and conversion, the W/O Pickering emulsion system even at lower stirring rate proceeded faster when considering the reaction time.

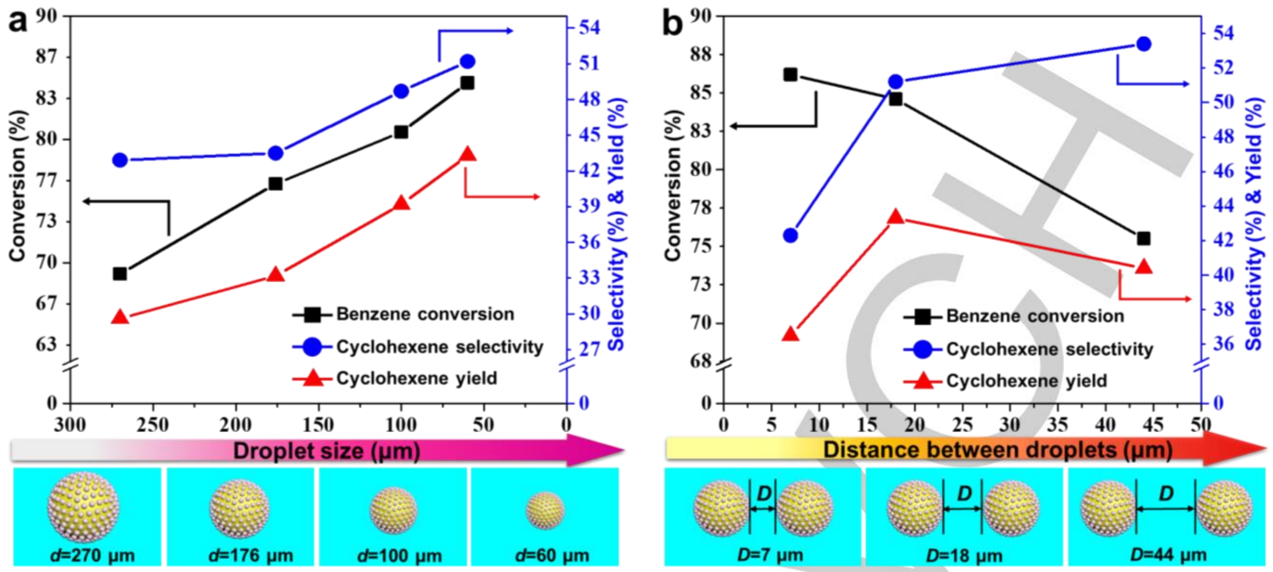

Figure 5. (a) Benzene conversion, cyclohexene selectivity and cyclohexene yield versus average droplet sizes in O/W Pickering emulsions. Pickering emulsions were formulated with different stirring rates (before reaction): 1000 rpm (*d*=270 μm), 3000 rpm (*d*=176 μm), 10000 rpm (*d*=100 μm) and 20000 rpm (*d*=60 μm). Raction conditions: 0.15 g catalyst, 15 mL benzene, 30 mL H_2O, 3 g $ZnSO_4 \cdot 7H_2O$, 5.0 MPa H_2, 140 °C and 700 rpm. (b) Benzene conversion, cyclohexene selectivity and cyclohexene yield versus average distances between two adjacent droplets in the O/W Pickering emulsion (homogenization at 20,000 rpm, 2 min). Reaction conditions: 0.15 g catalyst, 15 mL benzene, 5.0 MPa H_2, 140 °C, 700 rpm, a certain amount of $ZnSO_4 \cdot 7H_2O$ (1.5 g, *D*=7 μm; 3 g, *D*=18 μm; 4.5 g, *D*=44 μm).

This may be explained by the fact that the use of benzene as continuous phase is favorable to increase the solubility of H_2 in the reaction system.[20] The O/W Pickering emulsion system exhibited reaction rate slower than the W/O system because the continuous phase (water) has low solubility toward H_2, but slightly faster than the conventional biphasic system. Notably, the O/W Pickering emulsion system gave a cyclohexene yield of 43.3% at a benzene conversion of 84.6% within 60 min (Figure 4d). These results clearly demonstrate that the formulated O/W Pickering emulsion system outperforms two others in terms of the cyclohexene selectivity and yield even under low-speed agitation. It is worth noting that at the end of reaction, the droplets were still clearly observed (Figure S4). This is just a feature of Pickering emulsions, namely higher stability even at high temperatures due to the extremely high adsorption of particles at the oil/water interface, which is inaccessible for molecular surfactant-stabilized emulsions. Notably, the Pickering emulsion in which the Ru/TiO_2 particles were positioned just at the interfaces led to a low cyclohexene yield because the particle partially protrude in the oil phase, having no stagnant water layer (Figure S5).[17b]

Impact of emulsion droplet size

To clarify the role of Pickering emulsions, we firstly examined the O/W Pickering emulsion systems with different emulsion droplet sizes under the same conditions. The adjustment of emulsion droplet size was achieved by varying the stirring rate during emulsification since it is well established that the emulsion droplets size decreases as the shear rate increases in a certain range.[21] When the stirring rate was varied from 1000 to 3000, 10000 and 20000 rpm, the average size of the resultant droplets decreased from 270 to 176, 100 and 60 μm (Figure S6). Further increasing the stirring rate, the emulsion droplets size no longer downsized remarkably. Notably, although the droplet sizes in the above Pickering emulsion systems were found to undergo an increase after the reaction (414, 278, 189 and 135 μm, respectively), the order for the droplet size was not altered (Figure S7). The growth of droplets can be explained by the possibility that high temperatures accelerate Ostwald ripening and the polarity of oil phase is changed as products generated.[22] These Pickering emulsion systems with different droplet sizes led to different reaction outcomes, as presented in Figure 5a. When the average droplet size was changed from 270 to 176 and 100 μm, the corresponding benzene conversion increased from 69.1% to 76.4 and 80.6%, the cyclohexene selectivity increased from 42.9% to 43.5% and 48.7% and its yield increased from 29.6% to 33.2% and 39.2%. Impressively, when the droplets were further downsized to 60 μm, the benzene conversion further increased up to 84.6%, and the cyclohexene selectivity and yield increased up to 51.2% and 43.3%, respectively. These results highlight the impact of the droplet size on the conversion, selectivity and yield of the selective hydrogenation of benzene (Figure 5a).

For the O/W Pickering emulsion system, the catalysis reaction takes place in the continuous phase (outside the droplets) since the Ru/TiO_2 catalyst particles are distributed in water as discussed above. The oil−water interfacial area significantly increases with decreasing droplets size.[12] In parallel, as the droplet size reduces, the numbers of the droplets increase. Consequently, the average distance (*D*, Scheme 1b) between two adjacent droplets also declines from 81 to 53, 30 and 18 μm (calculation is provided in Supporting Information). The two factors all facilitate the benzene diffusion to the catalyst surface through the aqueous phase, resulting in the reaction acceleration and the increase in conversion. At the same time, the presence of excessive benzene molecules on the catalyst surface benefits desorption of cyclohexene molecules from the catalyst surface due to the competitive adsorption.[17c] As a result, the further hydrogenation of cyclohexene into cyclohexane is hindered, and high selectivity and yield of cyclohexene is thus obtained.

Impact of the droplet distance

We further investigated the influence of the average distance between two adjacent droplets (*D*) on the reaction outcome. The adjustment of droplet distance (*D*) was achieved by varying water volume while fixing the amount of benzene. As shown in Figure 5b, with varying the water volume from 15 to 30 and 45 mL, the corresponding mean distance (*D*) increases gradually from 7 to 18 and 44 µm (calculation is provided in Supporting Information). It should be noted that the increase in the volume of water also causes increase of droplet size from 50 to 60 and 100 µm (Figure S8). This is understandable because the emulsion droplet size is related to the volume of biphasic system when homogenized with the same stirring rate.[23] As the water amount increases, the benzene conversion decreases from 86.2% to 84.6% and then to 75.7%, and the cyclohexene selectivity increases from 42.3% to 51.2% and 53.4%, as shown in Figure 5b.

The changes in the benzene conversion and cyclohexene selectivity with the droplet distance (*D*) can be explained as follows. The average distance (*a*, Scheme 1b) between the oil-water interface and the catalyst particle increases as the droplet distance (*D*) increases. This means the transport distance of benzene from the oil droplet to the catalyst surface is increased. At the same time, with the increase in the droplet distance (as a result of increasing water volume), the H_2 transport from the gaseous phase to the catalyst surface is slowed down.[24] Therefore, the benzene conversion diminishes upon increasing the droplet distance (*D*). For cyclohexene, with increasing the droplet distance (water volume), the possibility of cyclohexene re-adsorbing back to the catalyst surface is reduced, avoiding its further hydrogenation. In parallel, the lowered H_2 transport rate also is beneficial for preventing further hydrogenation of cyclohexene.[17b] These factors work together, resulting in the high cyclohexene selectivity. Taking into account simultaneously the benzene conversion and cyclohexene selectivity with the droplet distance (*D*), it is easy to understand the change of the cyclohexene yield. These findings suggest that there is an optimal droplet distance for obtaining a maximum cyclohexene.

Impact of reaction temperature

Table S1 shows the impact of reaction temperature on selective hydrogenation of benzene in the O/W Pickering emulsion system. When the temperature was varied from 120 to 130, 140, 150 and 160 °C, the conversion of benzene decreased from 89.0% to 85.9%, 84.6%, 74.4% and 70.2%, and the cyclohexene selectivity increased from 44.6% to 47.0%, 51.2%, 53.4% and 54.1%. The decrease in reaction rate is attributed to the decreased solubility of H_2 in water. The cyclohexene selectivity is improved upon increasing the reaction temperature, which is explained by the possibility that the high temperature promotes cyclohexene desorption from the catalyst surface. Notably, in comparison to the conventional biphasic system, the benzene conversion and cyclohexene selectivity in the Pickering emulsion are more sensitive to the reaction temperature. (The conventional biphasic system, when the temperature was varied from 120 to 160 °C, the conversion of benzene decreased from 51.5% to 50.6%, and the cyclohexene selectivity increased from 50.5% to 54.1%).[25] This can be explained by the fact that the coalescence of Pickering emulsion droplets is aggravated with elevating reaction temperature, evidenced by the observation that the droplets size increases from 108 to 116, 135, 176 and 206 µm after reaction (Figure S9), while in the conventional biphasic system the droplets size largely relies on the agitation rate.

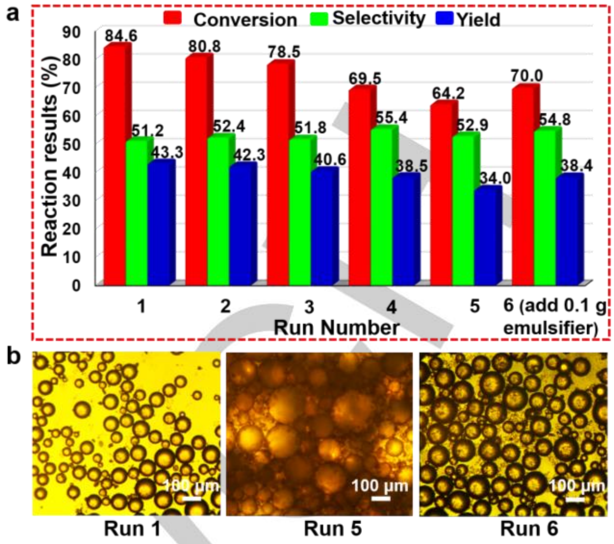

Figure 6. (a) Recycling results of the selective hydrogenation of benzene in O/W Pickering emulsion system; (b) optical microscopy images of O/W Pickering emulsion in the first reaction cycle, the fifth reaction cycle and the sixth reaction cycle. Reaction condintions are the same as those in Figure 4 except that 0.1 g fresh emulsifier was added in the sixth cycle.

Reusability

The reusability of the catalyst and solid emulsifier in the Pickering emulsion system is evaluated. At the end of the first reaction, the Pickering emulsion reaction system was demulsified through centrifugation, leading to phase separation. The upper layer of organics was isolated through decantation. The catalyst together with the emulsifier at the bottom layer were collected, and washed thoroughly deionized water. After being dried, the mixture of catalyst and emulsifier was directly used to the next reaction cycle. In the second reaction cycle, a Pickering emulsion with relatively uniform droplets could still be formulated, delivering the advantages of the solid emulsifier that is recyclable. As presented in Figure 6a, in the second reaction cycle, a cyclohexene yield of 42.3% with 52.4% selectivity was given. From the third to firth reaction cycles, the selectivity and yield for cyclohexene gradually declined slightly. For the fifth cycle, the cyclohexene yield and benzene conversion were reduced to 34.0% and 64.2%, respectively. We believe that these decreases in the cyclohexene yield and selectivity are caused by the loss of catalyst and the emulsifier due to the multiple transferring and separation. Emulsion droplets in the fifth cycle were observed to become larger due to the loss of emulsifier, in comparison to the first reaction. Therefore, in the sixth reaction, 0.1 g of fresh emulsifier was added as a supplement. As expected, the droplet size return to being as small as that in the first reaction cycle (Figure 6b). The cyclohexene yield and selectivity came back to 38.4% and 54.8%, respectively. After the six reaction cycles, the total TON for Ru reaches as high as *ca.* 5000 mol mol^{-1}, which is higher than that in the reported conventional biphasic counterpart system (1493 mol mol^{-1}).[19]

Conclusions

In summary, we have successfully demonstrated that the key parameters of biphasic catalysis reactions including the droplet size and droplet distance can be tuned with the Pickering emulsion strategy. Such a tuning is curial for the mass transport-sensitive, multistep catalysis reactions such as selective hydrogenation of benzene. As the case study shows, the Pickering emulsion system gave much higher cyclohexene selectivity (51.2%) and yield (43.3%) than the conventional biphasic system even under lower-speeded stirring. The catalyst together with the solid emulsifier could be recycled effectively. After six reaction cycles, the selectivity and yield of cyclohexene were still as high as 54.8% and 38.4%, respectively. Impressively, this strategy and the case study presented here will help to understand the behavior of biphasic catalysis and push biphasic reactions toward a more efficient and controllable level because it enables precise control of the key parameters of biphasic reactions.

Experimental Section

Preparation of methyl-functionalized TiO_2

P25 TiO_2 (1.0 g; dried at 110 ºC for 4 h) was ultrasonically dispersed into toluene (15 mL). A mixture of 0.4 mmol $(MeO)_3SiCH_3$ and 0.4 mmol $(C_2H_5)_3N$ were simultaneously added into the toluene system. After refluxing at 110 ºC for 4 h under N_2 atmosphere, the obtained material was isolated through centrifugation, washed five times with toluene and dried. The resultant methyl-functionalized TiO_2 nanoparticles are denoted as TiO_2-C(0.4). For TiO_2-C(4), 4 mmol $(MeO)_3SiCH_3$ and 4 mmol $(C_2H_5)_3N$ were used. Other procedures are the same as TiO_2-C(0.4).

Preparation of Pickering emulsions for catalysis reactions

Typically, 30 mL deionized water and 15 mL benzene were added into a flask containing a certain amount of catalyst, emulsifier and $ZnSO_4{\cdot}7H_2O$. After vigorously stirring with a homogenizer for 2 minutes, a Pickering emulsion (O/W or W/O) was obtained. Selective hydrogenation of benzene was carried out in a 100 mL autoclave. The autoclave was charged with prepared Pickering emulsion and sealed and then purged with H_2 three times to expel air and then the H_2 pressure was raised up to 5.0 MPa. The reaction was conducted at 140 ºC under stirring (700 rpm). The conversion, selectivity and yield were determined with Agilent 7890A gas chromatograph equipped with ATSE-30 capillary column and flame ionization detector (FID).

Acknowledgements

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Keywords: biphasic reactions• Pickering emulsions • droplet size • selective hydrogenation

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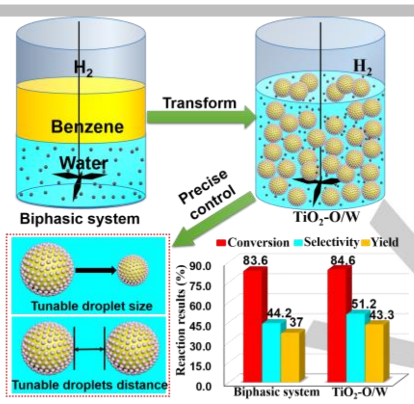
Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

An O/W Pickering emulsion system is developed for the selective hydrogenation of benzene to cyclohexene. Using this system, the reaction rate and selectivity of challenging biphasic reactions can be regulated by the rational adjustment of Pickering emulsion parameters including emulsion droplet size, droplet distance as well as emulsion type.



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