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Pd/g-C_3N_4 stabilized emulsion microreactor as a temporal hydrogen storage for full use of hydrogen from ammonia borane toward efficient alkene hydrogenation

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Abstract: Direct hydrogenation of C=C double bonds is a basic transformation in organic chemistry which is vanishing from simple practice due to the need for pressurized hydrogen. Ammonia borane (AB) has emerged as a unique hydrogen source due to its safety and high hydrogen content. However, in conventional systems the hydrogen liberated from the high-cost AB cannot be fully utilized. Herein, we develop a novel Pd/g-C_3N_4 stabilized Pickering emulsion microreactor, in which alkenes are hydrogenated in the oil phase with hydrogen originating from AB in the water phase, catalysed by the Pd nanoparticles at the interfaces. Notably, unit efficiency of hydrogen utilization is achieved within this microreactor, benefiting from the hydrogen storage capability of the emulsion *via* hydrogen concentrating at the Pd sites and in the liquid phases, whilst availabe for further hydrogenation until depletion. This buffer effect proves advantageous for more economical hydrogen utilization over conventional systems. The emulsion microreactor can be applied to a range of alkene substrates, with the conversion rates achieving > 95% by a simple modification.

Hydrogenation of C=C double bonds is one of the most important transformations in organic chemistry and is widely applied in pharmaceutical and fine chemical industries.[1] This transformation can be realized by direct hydrogenation with gaseous H_2,[2] requiring elevated hydrogen pressure, safety measures and specialist reactors.[3] Alternatively, the transformation can be achieved by transfer hydrogenation, which refers to the transfer of hydrogen to the target molecule from a liquid hydrogen donor, such as an alcohol.[4] This approach is environmentally more benign and is recieving increasing attention.[4b,5] Recently, ammonia borane (NH_3BH_3, AB) has proven to be an excellent hydrogen source owing to its stability, aqueous solubility and high hydrogen content (19.4 wt%).[6] It is convenient and useful for the efficient hydrogenation of C=C, C=N and N=O in the presence of Pd catalysts, where the Pd catalyses both the AB hydrolysis and the hydrogenation.[7] One potential drawback with using AB is that the cost is still quite high.[8] Another drawback that needs redressing is that the H_2 produced from AB partly escapes from the conventional reaction system due to local H_2 overproduction, resulting in a waste of the reagent. In this context, the full use of AB for organic transformations is a significant task.

Pickering emulsions are emulsions stabilized by solid particles rather than surfactant molecules, in which oil/organic solvent or water is dispersed into the other phase in the form of micrometre-sized droplets.[9] Taking advantage of the unique organic-solid-water morphology, Pickering emulsions can convert traditional biphasic reactions to a macroscopically homogeneous emulsion phase, with the incompatible reactants confined in either oil or the aqueous phase.[10] This approach exposes an abundant reactive interface surface area and is free of extra solvents or surfactants/transfer agents often required to make the reaction system potentially miscible. In a recent study, it has been demonstrated that graphitic carbon nitride (g-C_3N_4) can serve as a low cost Pickering stabilizer.[11] Unlike the commonly used SiO_2 emulsifier, no surface modification of g-C_3N_4 is required. In addition, g-C_3N_4 is a well-known support for the immobilization of metal nanoparticles and molecular catalysts.[12] It also posseses excellent stability across a broad range of conditions and solvents.[13]

Herein, Pd nanoparticles (NPs) were loaded onto g-C_3N_4 sheets by simple photo-deposition to endow the material specific catalytic activity while keeping the emulsifying capability. The obtained Pd/g-C_3N_4 was then employed to stabilize Pickering emulsion for conducting an efficient alkene hydrogenation in the oil phase, where the hydrogen was generated *in situ* from AB in water, with Pd NPs acting as a bifunctional catalyst located at the interfaces. It is shown that the efficiency of hydrogen utilization in this Pickering emulsion system can reach unity, i.e. the added AB is used without loss for the hydrogenation occurring in the other phase. Kinetic insights and *in situ* observation show that the emulsion is capable of temporally storing hydrogen that is not directly consumed, and the stored hydrogen reacts with the alkene afterward until depleted.

Figure 1a provides a TEM image of 2 wt% Pd/g-C_3N_4. Pd NPs have a size distribution centered at 2~6 nm and were uniformly dispersed on the g-C_3N_4 support. HRTEM imaging (Figure 1b) of a single Pd nanoparticle measured a fringe spacing of 0.225 nm, which corresponds to the (111) planes of face-centered cubic palladium. Measurments of the g-C_3N_4 sheet supports reveal that they were typically weakly ordered. Elemental line-scans across two different locations shows the distribution of the Pd element, which corresponds with the dark-field TEM image (Figure 1c). The chemical nature of the

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supported Pd NPs was studied by X-ray photoelectron spectroscopy (XPS). Fitted XPS spectra (Figure 1d) of Pd $3d_{3/2}$ and $3d_{5/2}$ orbitals are strong evidence that the Pd NPs were predominantly in metallic state (Pd^0), with the presence of a small proportion of PdO and PdO_2.[14] Importantly, the Pd/g-C_3N_4 composite can act as an efficient stabilizer for Pickering emulsions, an effect originating from the interfacial activities of g-C_3N_4. As shown in Figure 1e, Pickering emulsions were readily generated by shaking the mixture of styrene and aqueous dispersions of Pd/g-C_3N_4 manually. By dyeing the water phase with methylene blue it was confirmed that an oil-in-water emulsion is formed, i.e. styrene constituted the dispersed droplets and water as the continuous phase (**Figure S1**).

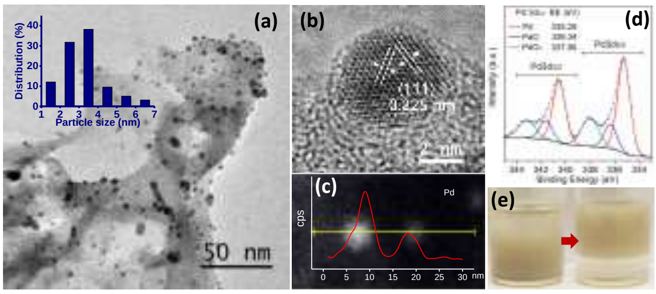

Figure 1. Characterizations of 2 wt% Pd/g-C_3N_4: (a) TEM image and size distribution, (b) HRTEM image, (c) elemental line profile of Pd, and (d) XPS spectrum of Pd $3d_{3/2}$ and $3d_{5/2}$ orbitals. (e) Photograph of styrene-water Pickering emulsion stabilized by 2wt% Pd/g-C_3N_4 before (left) and after (right) emulsifying.

Figure 2a shows a light microscopy image of the as-prepared emulsion, exhibiting numerous oil droplets with sizes in the range of 100–400 μm. The droplet surfaces were densely covered by the Pd/g-C_3N_4 particles. Employing a styrene-Pd/g-C_3N_4-water emulsion system, we then conducted a hydrogen liberation-hydrogenation tandem reaction using AB as the hydrogen source, as schematically displayed in Figure 2b. In a typical procedure, 2 mg of Pd/g-C_3N_4 was dispersed in 1 ml of deionized water by sonication, and then 1 ml of styrene was added and emulsified by manual shaking. Afterwards, 0.5 ml of AB aqueous solution (8 mg/ml) was injected into the emulsion to initiate the reaction at 40 °C. Note that styrene was in far excess compared to AB in this reaction. In this case, a maximum 0.35 mmol of H_2 (H_2 is used for convenience purposes to denote the hydrogen from AB and does not necessarily mean gaseous H_2 unless noted) could be produced by AB, ideally leading to the generation of 0.35 mmol of ethylbenzene. Different Pd loadings were examined to assess the catalytic activity of the Pd/g-C_3N_4 nanocomposite. As shown in Figure 2c, experiments with 0.5 wt% Pd loading (**Figure S2a**) show relatively low activity, and 0.31 mmol of ethylbenzene was obtained after 18 h reaction time. For the nanocomposites with 2 and 5 wt% Pd loading (TEM images shown in Figure S2b), the reactions proceeded much more quickly, and 0.32 mmol of ethylbenzene was already reached in the first 8 h. Then the reactions slowed down owing to the consumption of AB, and 0.35 mmol of ethylbenzene was eventually generated. In this regard, the H_2 released from AB (3 equiv. of AB) fully reacted with styrene; in other words, the hydrogen utilization efficiency (HUE), defined as HUE= $[mol\ of\ ethybenzene/3 \times (mol\ of\ AB)] \times 100\%$, reached unity (>99%). Control experiments showed that no ethylbenzene was detected when only g-C_3N_4 was used, verifying that Pd provides the catalytic sites for the coupled reactions.

Next, a series of reference and blind experiments were conducted for better understanding the reactions in the Pickering emulsion microreactors. As shown in Figure 2d, when AB was replaced by 0.35 mmol of gaseous H_2 (outside the emulsion system), very low amount of ethylbenzene and HUE were observed, due to limited mass transfer from gas to the liquid phases (entry 2). Additionally, when AB was used but no emulsification was applied, 0.11 mmol of ethylbenzene and a HUE of 33% was obtained, resulting from the limited macro-interface between the two immiscible phases (entry 3). Applying stirring (500 rpm) led to slightly increased interface area and thus the catalytic performance slightly improved (entry 4). In another experiment, ethanol was added to generate a miscible, homogenous solvent for the reactions. In this condition, the catalytic performances were still low, achieving only 0.15 mmol of ethylbenzene and a HUE of 45% (entry 5). These comparison studies confirmed the efficacy of a combined dehydrogenation-hydrogenation in the emulsion microreactor. This statement can also be verified by using water-soluble alkenes (allylamine and 2,5-dihydrofuran) for more efficient hydrogenation in Pickering emulsions than in normal aqueous solutions (**Figure S3**).

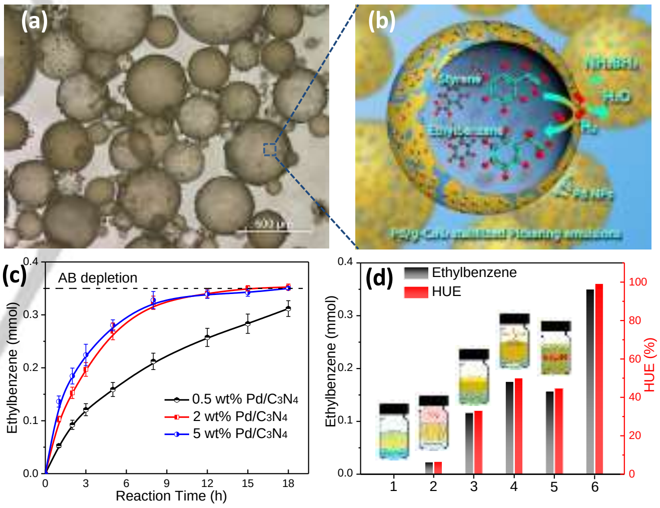

Figure 2. (a) LM image of Pickering emulsions made from 1 ml of styrene and 1 ml of 2 mg/ml 2 wt% Pd/g-C_3N_4 dispersion. (b) Schematic illustration of AB hydrolysis combined with styrene hydrogenation in the Pickering emulsion system, catalyzed by the Pd NPs at the droplet interfaces. (c) Time-dependent ethylbenzene generation over 0.5, 2 and 5 wt% Pd/g-C_3N_4, respectively. (d) Control group experiments for hydrogenation: entry 1. g-C_3N_4 as catalyst; 2. AB replaced by 0.35 mmol of gaseous H_2; 3. without emulsifying; 4. no emulsifying but stirred at 500 rpm; 5. dissolving whole emulsion system in ethanol; 6. typical procedure. Note that all these experiments were conducted for 18 h.

In the next set of experiments, the detailed kinetics of the dehydrogenation and hydrogenation reaction were monitored separately at different temperatures (30, 40 and 50 °C, **Figure 3a-c**). Both the dehydrogenation and hydrogenation became faster at higher temperatures, whilst all the evolved H_2 from AB was consumed by styrene, generating 0.35 mmol of ethylbenzene at each temperature. It is very interesting to note

10.1002/anie.201809882

that the hydrogenation lags behind the hydrogen evolution in the middle of the reaction, especially at 30 and 40 °C, leading to varied HUE against reaction time (**Figure S4**). We can derive from the profiles that the hydrogenation reaction was slower than the hydrogen evolution at the initial stage of the reactions. After then, during the middle and final stage of the reactions, the hydrogenation rate turned faster than the hydrogen evolution rate, according to the derivatives of the profiles. This should be owing to the consumption of AB and accumulation of hydrogen. Moreover, the gap between the kinetic profiles became narrower when the temperature was raised to 50 °C, with the reaction rate of dehydrogenation and hydrogenation becoming very close. These results indicate that in this emulsion-based biphasic reaction, the majority of the hydrogen from AB is consumed by the subsequent styrene hydrogenation, catalysed by the interfacial Pd sites via direct hydrogen transfer (Equation S1). The abundant reactive and catalytic sites at the droplet surfaces are highly beneficial to the coupled reactions. Nevertheless, a small amount of locally overproduced hydrogen is not available to immediately react with styrene, which form gaseous H_2 and then react with the styrene molecules (Equation S2 and S3).

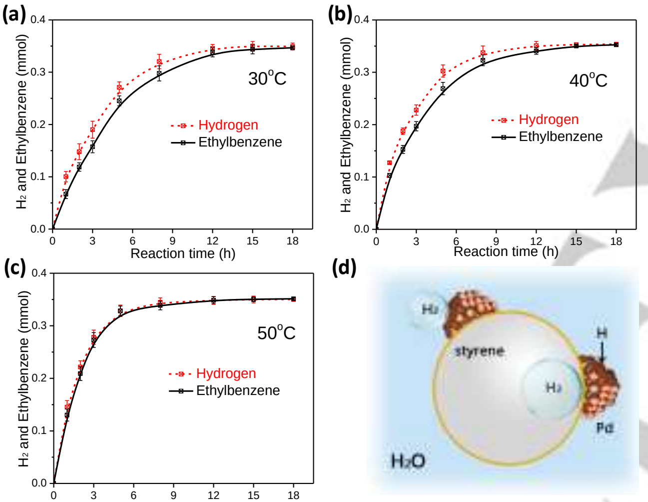

Figure 3. Kinetic study of hydrogen evolution and hydrogenation reaction at (a) 30 °C, (b) 40 °C, and (c) 50 °C. (d) Schematic demonstration of the hydrogen buffer effect of the Pd/g-C_3N_4 Pickering system. Pd NPs are enlarged for better visualization.

Based on the above discussion and considering the overall HUE reached unity at the end of the reactions, we propose that a small fraction of the hydrogen produced at the beginning of the reaction which is not instantly consumed by the slower hydrogenation reaction did not escape, but conserved in the system, i.e. within the Pickering hybrid system which is effectively acting as a hydrogen buffer. It is well documented that Pd is able to chemosorb a large number of hydrogen.[15] These chemisorbed hydrogen are highly active and can react with styrene afterwards. The second hydrogen storage mechanism is hydrogen microbubbles, which – due to the viscosity and roughness of the Pickering system – can stay trapped at the g-C_3N_4 particle surface in the continuous aqueous phase (**Figure S5**) as well as in the dispersed organic droplets. As shown in **Figure S6**, micro H_2 bubbles were formed in the styrene droplets after injection of AB, and the bubbles grew a bit larger in the next 10 min. Interestingly, the bubbles shrink afterwards and then completely vanished, owing to the reaction with styrene. The hydrogen buffer effect of the Pd/g-C_3N_4 stabilized Pickering emulsion is schematically shown in Figure 3d.

Further experiments prove that the hydrogen storage capacity of the emulsion is related to the amount of the Pd/g-C_3N_4 stabilizer. As shown in **Figure 4a**, the ethylbenzene amount decreased to 0.19 and 0.09 mmol when 1 mg and 0.5 mg of catalyst was used, respectively, which was expected due to the reduced catalyst amounts. More importantly, the HUE concurrently reduced to 54% and 27%, respectively, even when the reaction was prolonged to 45 h (**Figure S7**). These results strongly imply that in these conditions, the liberated H_2 escaped from the emulsion system and did not participate further in the hydrogenation, most likely resulting from insufficient Pd adsorption sites and emulsion stabilizer (**Figure S8**). Moreover, the hydrogen storage capability can be taken advantage of to improving the transformation rate of styrene, and meanwhile maintaining unity HUE. As shown in Figure 4b, when the AB loading was increased to 8 and 12 mg, 0.7 and 1.05 mmol of ethylbenzene was obtained, respectively. It is worth pointing out that the gap between the kinetic profiles of hydrogen evolution and ethylbenzene generation became larger at higher AB amounts, which is reasonable as more hydrogen was released. Correspondingly, the profiles almost totally matched when the AB input was down to 2 mg.

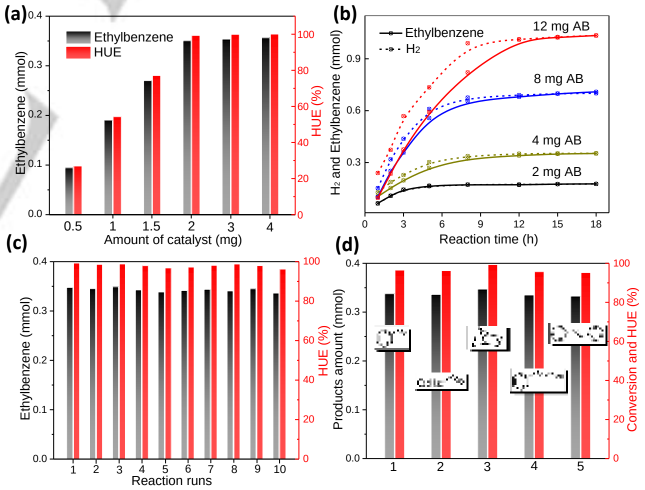

Figure 4. (a) Ethylbenene production and HUE in the presence of different amount of 2 wt% Pd/g-C_3N_4 at 40 °C. (b) Kinetic study of dehydrogenation and hydrogenation with different amount of AB over 2 mg of 2 wt% Pd/g-C_3N_4 at 40 °C. Dashed lines illustrate hydrogen amount and solid lines illustrate ethylbenzene amount. (c) Reusability test of 2 wt% Pd/g-C_3N_4 catalyst for 10 emulsification-catalyzation cycles at 40 °C. (d) Hydrogenation of various alkene substrates in the Pickering emulsion system. Reaction conditions: 0.35 mmol of substrates dissolved in 1ml of cyclohexane (for substrates 1, 2, 3) or 1 ml of toluene (for substrates 4, 5) as oil phase, 4 mg of AB, 18 h, 40 °C (for substrates 1, 2, 3,4) or 80 °C (for substrate 5).

Furthermore, the recyclability of the Pd/g-C_3N_4 catalyst in the current Pickering emulsion microreactor was evaluated. After simply washing, the nanomaterials can be reused for the next-cycle emulsification and catalytic reaction (**Figure S9**). As shown in Figure 4c, high catalytic activity toward the hydrogen evolution−hydrogenation reaction was well maintained up to 10 cycles, with no decline of HUE and ethylbenenze production. TEM observation and XPS measurement demonstrate that after 10 cycles, the Pd NPs grew a bit larger, while their chemical state remained unchanged (**Figure S10**). Turnover frequency (TOF) $[(mol\ of\ ethylbenzene/mol\ of\ Pd)\ per\ hour]$ was determined and only showed slight decrease upon each catalysis cycle (**Figure S11**), probably because of the slow growth of Pd NPs, indicating the superior reusability of the Pd/g-C_3N_4 catalyst.

Finally, the conversion rate of alkene can be substantially promoted by simply modifying the Pickering emulsion microreactor. Briefly, cyclohexane was used as a solvent to dissolve 0.35 mmol of styrene and then emulsified with Pd/g-C_3N_4 aqueous dispersion, followed by addition of AB (0.117 mmol) as described above (see Supporting Information for details). In this situation, the reagents can fully react with each other and resulted in a final conversion of 97% (Figure 4d, entry 1). More importantly, this modification enabled us to largely extend the range of the alkene substrates, as some of the educts cannot be directly emulsified. As shown in entry 2–5 (Figure 4d), four substrates with very different types of C=C double bonds were chosen for hydrogenation, and high conversion rate and HUE (95~99%) were achieved.

In summary, we have presented a novel Pd/g-C_3N_4 stabilized Pickering emulsion microreactor to couple hydrogen generation from AB with hydrogenation of alkenes at the oil-water interfaces of the droplets. The hydrogen utilization efficiency can reach unity in such an emulsion system, mainly due to the localized production, storage, and consumption of hydrogen on the Pd NPs. Detailed analysis and observations revealed that the Pickering emulsion can effectively store hydrogen *via* adsorption in the Pd nanoparticles and microbubble formation within the liquid phases. The stored hydrogen then reacted with alkene molecules until complete consumption. This hydrogen storage capability obviously played a key role for the efficient use of hydrogen. The Pd/g-C_3N_4 catalyst illustrated excellent reusability and tunred out to be rather generally applicable to various alkene molecules. Importantly, the conversion rate of alkene can reach > 95% by simply modifying the Pickering emulsion microreactors. This work opens a new avenue for developing more economical and efficient hydrogenation proccesses for the production of a wide range of valuble chemicals.

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Keywords: graphitic carbon nitrides • Pd nanoparticles • emulsion microreactors • hydrogenation

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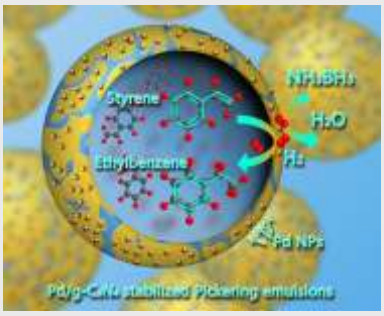
COMMUNICATION

A novel Pd/g-C_3N_4 stabilized Pickering emulsion microreactor is developed to conduct alkene hydrogenation using ammonia borane as the hydrogen source. This system can serve as a general hydrogen buffer space, leading to unit efficiency of hydrogen utilization. This emulsion microreactor provides more economical hydrogen utilization over conventional systems.



*Chenhui Han, Peng Meng, Eric R. Waclawik, Chao Zhang, Xin-Hao Li, Hengquan Yang, Markus Antonietti and Jingsan Xu**

Page No. – Page No.

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