Pausing a stir: heterogeneous catalysis in "dry water"†

Benjamin O. Carter, Dave J. Adams and Andrew I. Cooper*

The highly distributed gas–liquid interface in "dry water" powder can be used to greatly increase the kinetics of a gas–liquid heterogeneous catalytic hydrogenation, in the absence of any applied mixing.

The rate of heterogeneous gas–liquid reactions is often limited by contact between the gas and liquid phases. Indeed, for solid catalyzed gas–liquid reactions, mass transfer effects are usually crucial, especially if reaction at the solid catalyst surface is fast.[1,2] To increase gas–liquid contact, a number of engineering solutions have been developed,[3] including sparging,[4] packed bed reactors,[5] trickle bed reactors[5] and the careful design of impellers[6] and other stirrers to maximize mixing. For stirred systems, there also exists a measurable correlation between the stirring power input per unit liquid, and the gas–liquid volumetric mass transfer coefficient.[7,8] Hence, an opportunity exists to improve the energy-efficiency of gas–liquid reactions if the power input through stirring can be reduced without affecting reaction rate.

Dry water (DW) is a water-in-air inverse foam, produced by mixing water with hydrophobic silica particles (H18, Wacker Chemie) in a conventional domestic blender.[9] This produces a free-flowing powder which can contain up to 99% water, comprised of water microdroplets where coalescence is prevented by a coating of silica. The droplet size in DW is typically of the order of 50 μm. We have recently demonstrated that the small size of these water domains results in a marked increase in the kinetics of methane gas hydrate formation when DW is cooled under a pressure of methane.[10] This increase in the clathration kinetics can be ascribed to the much greater contact between methane and DW and its greatly enhanced surface area to volume ratio in comparison with the equivalent reaction in bulk water. Here, we demonstrate that this concept can also be used to carry out heterogeneous gas–liquid reactions in DW. This represents a novel method of carrying out heterogeneous gas–liquid reactions, without the need to stir or otherwise agitate the reaction. This could in some cases represent a significant energy saving, particularly for reactions which occur at moderate temperatures.

The heterogeneous hydrogenation of maleic acid to succinic acid represents a good test reaction, having been extensively studied.[11–13] A number of heterogeneous catalysts have been used, including those based on Pd, Pt or Ru. In these cases, efficient mixing between gas and liquid has been achieved by, for example, sparging hydrogen directly beneath the impeller.[12] The importance of the impeller speed was shown by the dependence of the initial rate of hydrogenation on the speed of agitation.[1]

A free-flowing DW-like powder can be prepared by blending an aqueous solution of maleic acid (110 mL, 0.075 M) with H18 silica (5.79 g, 5 wt% based on water) and 5 wt% Ru/Al₂O₃ catalyst (0.1790 g, 1.625 gL⁻¹), Fig. 1. After blending (37 000 rpm, 90 s), the droplet size was found to be around 26 ± 17 μm as estimated by optical microscopy. The powder formed was indistinguishable from DW formed from neat water, both in terms of its flow characteristics and stability. The material could be stored without loss of water by evaporation in plastic bottles for up to 1 month without coalescence of the droplets and the appearance of a bulk water phase. Fig. 1c and 1d show that the size distribution of the aqueous droplets was unaffected by the addition of the catalyst. It is interesting to note that such a powder can still be prepared despite the relatively high concentration of maleic acid present in the system, and that the mixture remains stable at these concentrations for at least one month. Similarly, a free-flowing powder was formed on blending a 0.075 M solution of succinic acid in the presence of H18 silica (data not shown).
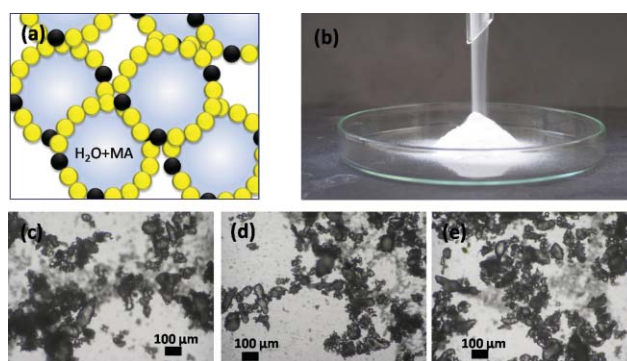

Fig. 1 (a) Schematic of DW droplets containing maleic acid, surrounded by H18 silica and Ru/Al₂O₃ particles (black). (b) Photograph showing the DW containing maleic acid flowing through a funnel. (c) Microscope images (100× magnification) showing DW containing (c) maleic acid as formed; (d) maleic acid in the presence of Ru/Al₂O₃ catalyst; (e) maleic acid and Ru/Al₂O₃ after 1 h at 70 °C in the presence of hydrogen (20.7 bar).

After preparation of the maleic acid DW, hydrogenation was carried out by pressurizing the DW (20 g) with hydrogen (20.7 bar) in a 50 mL capacity stainless steel autoclave

Department of Chemistry and Centre for Materials Discovery (CMD), University of Liverpool, Crown Street, Liverpool, L69 7ZD, UK.
E-mail: aicooper@liverpool.ac.uk; Fax: +44 (0)151 794 3588; Tel: +44 (0)151 794 3548
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(Parr Instruments). No stirring was used. The reaction was heated to 70 °C prior to introduction of hydrogen. To monitor conversion with time, a series of reactions were performed, stopped at pre-determined time-intervals. The elevated temperature, pressure of hydrogen, and presence of succinic acid product did not affect the stability of the DW, with the material remaining as a free-flowing powder with similar droplet size throughout (Fig. 1e).

The DW mixture was then centrifuged (5000 rpm, 10 min) to coalesce the droplets and hence to separate the solid and aqueous components. The conversion of maleic acid to succinic acid was measured using ^{1}H NMR. Control experiments demonstrated that this method accurately reflected the composition of the solution, with no preferential adsorption of either maleic acid or succinic acid to the silica. The results are shown in Fig. 2. For comparison, the results for reactions of a bulk, unstirred aqueous solution of maleic acid with hydrogen in the presence of Ru/Al$_2$O$_3$ (*i.e.*, not pre-formed into DW) are also shown. We have also included data for reactions carried out in the absence of hydrophobic silica, but in an impeller-stirred pressure vessel. The conditions used here mirror those used elsewhere,[12] albeit with an elevated loading of catalyst (1.63 gL^{-1}). At lower catalyst loadings (0.065 gL^{-1}), the DW system gave irreproducible data across a given reaction period, which we ascribe to uneven distribution of the catalyst across the DW gas–liquid interface.
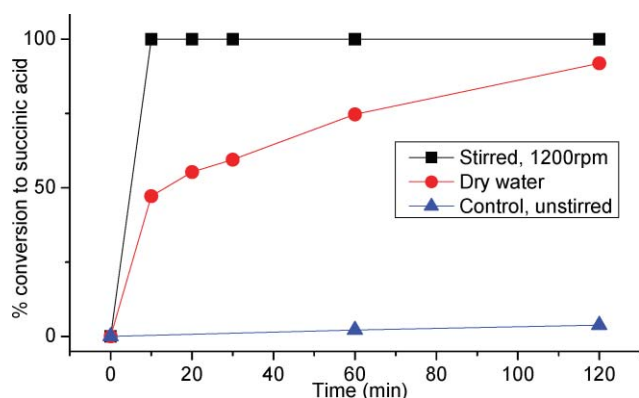

Fig. 2 Kinetic hydrogenation data for unstirred control reaction (▲), DW (●), and for stirred control reaction (■). All experiments were carried out at 70 °C, 20.7 bar.

As can be seen in Fig. 2, a very low conversion of maleic acid to succinic acid was achieved for an unstirred bulk mixture of silica, maleic acid solution and catalyst. This is as expected for a poorly mixed, heterogeneous reaction. Stirring the system during reaction in the absence of silica results in fast conversion to succinic acid, as expected.[12] Interestingly, for the DW system, greatly enhanced kinetics of succinic acid formation were observed over the control, though these kinetics were somewhat slower than observed for the comparable stirred reaction.

The activity of recovered Ru/Al$_2$O$_3$ was tested by re-blending recovered catalyst and silica with fresh maleic acid solution, followed by a 1 h hydrogenation. The resulting samples were

found to be increasingly aggregated and less flowable, possibly due to changes in the surface chemistry of the nanoparticles.

From an energy perspective, the DW method presented here requires just 30 s of blending at 19 000 rpm in addition to a centrifugation step. The centrifugation step is however readily circumvented since the DW droplets can be coalesced in other ways, for example by the addition of a small amount of methanol. Although we have not yet made quantitative comparisons, this is likely to compare very favourably with the energy input required to stir the reaction at 1200 rpm for the duration of the reaction. It is also clear, however, that for this reaction it is necessary to heat the system for a much longer time to achieve comparable conversions (Fig. 2). Although this may offset any energy gains in terms of stirring for this particular reaction, it suggests that the DW method could be more attractive, for example, in reactions which occur at lower temperatures. Additionally, for larger scale reactions which suffer from poor heat exchange, these may be carried out slower than the intrinsic reaction rate to offset this disadvantage. In such a case, a DW approach may prove more energy efficient despite a slower running time.

This catalytic hydrogenation serves as a proof of concept for the use of a distributed DW gas–liquid interface in multi-phase fluid reactions. The concept may be applicable to a number of aqueous-based gas–liquid reactions. For example, more viscous reaction mixtures require a much greater power input in terms of stirring and such systems might perform more favorably in a DW form. Indeed, we have recently prepared DW containing gelling agents which involve mixtures which are extremely viscous and hard to stir but which can be blended into stable DW form in as little as 60 s.[14] Additionally, one can envisage a heterogeneous catalyst that could also act as the solid DW stabilizing agent. We also suggest that DW may impart greater ease of handling to some reactants.

In summary, we have used a "dry water" distributed gas–liquid interface to produce a reaction mixture with a high surface area to volume ratio. We have demonstrated that this system can be used to conduct catalytic hydrogenation without the need for stirring during reaction. This new concept requires considerable investigation in terms of scale-up potential, but could in time be applied to specific gas–liquid reactions in order to improve the overall energy efficiency.

Acknowledgements

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