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By *Fabing Su, Christopher L. Bray, Bien Tan,* and *Andrew I. Cooper**

Clathrate hydrates are cagelike, hydrogen-bonded structures that have potential for the storage of H_2 and other gases close to ambient temperatures.[1] The potential environmental impact of clathrate hydrates is low because they consist mostly of water. There are, however, three significant barriers to real applications in the case of H_2: (i) relatively low H_2 storage capacities; (ii) high pressures required for clathrate formation and stabilization; and (iii) slow, non-stochastic kinetics associated with enclathration. The pressure at which H_2 enclathration occurs can be significantly reduced from 200 to 7 MPa by adding a stabilizer, such as tetrahydrofuran (THF).[2] Recently, Lee et al.,[3] reported a gravimetric H_2 storage capacity of around 4 wt % at 12 MPa/270 K at low THF concentrations, although subsequent studies suggest lower storage capacities (up to ca. 1 wt %) under similar conditions.[4,5] Other H_2 clathrate systems also show promise,[6] for example semiclathrate hydrates based on ammonium salts,[7] which form at modest pressures and can show high stability at temperatures > 285 K. The search for enhanced clathrate hydrates for H_2 storage continues, although thus far it has proven difficult to combine both high storage capacities and moderate pressures in a single system.

Even if the storage capacity, pressure, and clathrate stability issues are successfully addressed, a generic practical limitation may prove to be the kinetics of clathrate formation in the bulk. For example, the formation of D_2O–H_2 clathrate occurs very slowly and full conversion is not achieved even after 5–10 days in some cases.[8] In general, the formation of H_2–THF–H_2O clathrates may require several days.[5] Mass diffusion can be enhanced by increasing the surface-to-volume ratio of clathrate hydrates by using small crushed ice particles[5] or by dispersing the clathrate hydrate on silica beads,[3] or in the case of CH_4, on activated carbon.[9] However, the use of crushed ice particles is inconvenient and, for multiple storage/release cycles, the material would revert to the bulk state upon melting. Likewise, silica beads and activated carbons have, in this context, relatively low pore volumes ($<2\,cm^3\,g^{-1}$) and high

bulk densities; hence, such supports may compromise the gravimetric H_2 storage capacity.[3] Other methods to accelerate clathrate formation, such as efficient mechanical mixing or multiple temperature cycles, can be achieved in the laboratory but are likely to be unsuitable for practical applications such as onboard storage. As such, the development of a rechargeable, static (unmixed) clathrate-based gas storage system with accelerated formation kinetics that does not compromise the H_2 storage capacity remains a major challenge.

Here, we demonstrate a method that dramatically improves the kinetics and reusability for gas clathrates by using an ultralow-density, emulsion-templated polymerized high internal phase emulsion (polyHIPE) material as support.[10–12] The methodology is illustrated for H_2 but should in principle be applicable to a broad range of gases and gaseous mixtures such as natural gas. Figure 1a shows a scanning electron microscopy (SEM) image of the macroporous polyHIPE, which consists of open cells interconnected by pore windows. The pore size distribution derived from mercury porosimetry (inset, Fig. 1a) exhibits a narrow peak centered at 9.1 μm. The Brunauer–Emmett–Teller (BET) surface area was 230 $m^2\,g^{-1}$. Figure 1b schematically illustrates the clathrate hydrate dispersed within the porous polyHIPE material.

Although these polystyrene-based materials are very hydrophobic, a 5.56 mol % aqueous solution of THF has sufficient wettability for a supported film to form within the interconnected pore structure. Thus, a large interfacial area and short diffusion path (on the order of a few micrometers) is available for gas clathrate formation. A key feature of the material is the interconnected pore structure and the very low bulk density (0.056 $g\,cm^{-3}$). As such, it is possible to support at least 20 g of the THF–H_2O solution on just 3 g of polyHIPE; that is, a gravimetric "penalty" of 13% relative to the bulk THF–H_2O system. Moreover, it is likely that the amount of polymer required to disperse a given volume of solution could be further reduced by rendering the material more hydrophilic (see discussion below).

Figure 2 shows the cooling/heating curves for the H_2–THF–H_2O system (5.56 mol % THF based on H_2O), with and without the emulsion-templated support. With no support (curve A), the *P–T* relationship for H_2 in the system approximated to the ideal gas law during the continuous cooling/heating cycle. There was no evidence for H_2 clathrate formation or dissociation under these conditions (bulk solution, no crushed particles or mixing, temperature

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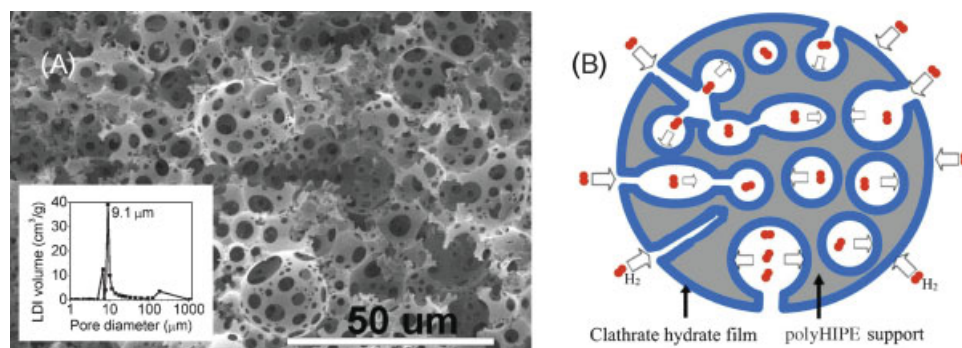E-mail: aicooper@liverpool.ac.uk

Figure 1. A) SEM image and pore size distribution (inset) for macroporous polyHIPE (50 μm scale bar). B) Schematic illustration of clathrate hydrate dispersed on the polyHIPE support.

ramp = 2.5 K h^{-1}). By contrast, there was distinct evidence for clathrate formation and subsequent dissociation in the presence of the polyHIPE support (curve B), as shown by the dramatic pressure drop upon cooling and the rapid pressure rise upon heating, respectively. This behavior is similar to that reported recently for H_2 enclathration in semiclathrate hydrates.[7] Clathrate formation occurred during cooling between 277.1–275.2 K with an associated exotherm. The pressure drop with temperature recovered to a linear trend below 275.2 K, indicating completion of the H_2 clathrate formation process.[7] During warming, clathrate dissociation commenced at around 275.2 K and was completed at 282.3 K. The formation of H_2 clathrate (in contrast to the absence of formation in the bulk) can be attributed to the polyHIPE support, which disperses the H_2–THF–H_2O clathrate phase. The H_2 enclathration capacity derived from the pressure drop, ΔP (1.1 MPa), at 270.0 K was estimated to be 0.18 wt % relative to the mass of H_2O and THF (using the ideal gas law) or around 0.15 wt % as calculated using GasPak v3.41 software. Volumetric release experiments in which the H_2 clathrate was stabilized at lower temperatures showed higher H_2 storage

capacities of 0.4–0.5 wt %,[13] very similar to the values reported previously by Strobel et al.,[5] when crushed and sieved THF-ice particles (45 or 250 μm) were employed (see Supporting Information, Table S1).

Figure 3 shows kinetic plots for H_2 enclathration in preformed THF–H_2O hydrate (5.56 mol % THF) at 270.0 K, both with and without the polyHIPE support. A baseline plot was obtained using an equivalent volume of glass beads (20.0 cm^3) plus polyHIPE (3.0 g): no pressure drop occurred after the initial temperature equilibration immediately following rapid H_2 addition up to 11.6 MPa (curve A). With no polyHIPE and in the presence of the THF–H_2O hydrate, a small, gradual pressure drop occurred over >1200 min (curve B), consistent with slow H_2 uptake in the bulk THF–H_2O hydrate.

In the presence of the polyHIPE, a larger, much more rapid pressure drop was observed (curves C–G). The rate of H_2 uptake was found to increase over two charge-discharge cycles (curves C and D) and thereafter to become reproducible (curves E–G). We ascribe this to the limited wettability of these hydrophobic polystyrene materials and enhanced dispersion of the H_2O–THF solution throughout the structure
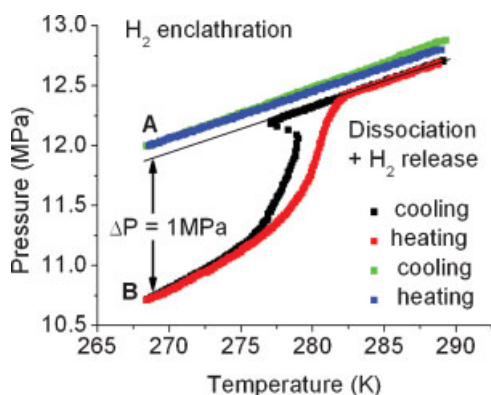

Figure 2. P–T plots for H_2–THF–H_2O ternary system during cooling and heating (temperature ramp: 2.5 K h^{-1}). A) without polyHIPE (for clarity, the curve was shifted vertically by +0.4 MPa). B) with polyHIPE support (20.0 g THF–H_2O solution, 5.56 mol % THF; 3.0 g polyHIPE).
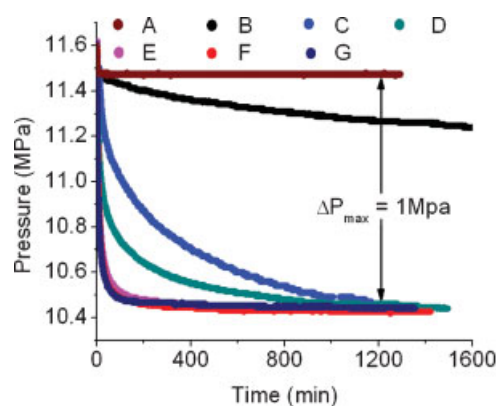

Figure 3. Kinetic plots for H_2 encapsulation in THF–H_2O clathrate hydrate supported within polyHIPE at 270.0 K. A) 20.0 cm^3 glass beads and 3.0 g polyHIPE, no H_2O–THF (baseline). B) 20.0 g H_2O–THF solution, no polyHIPE support. C) 20.0 g solution, 3.0 g polyHIPE (1st run). D–G) 20.0 g solution, 3.0 g polyHIPE (2nd–5th runs).

after the first three freeze–thaw cycles. This recyclability contrasts with crushed or spray-frozen H_2O–THF hydrate particles (data not shown) where a kinetic enhancement is observed for one cycle, after which the kinetic behavior reverts to the slow, bulk uptake (curve B) if the particles are allowed to melt during gas release.

The maximum H_2 pressure drop (ΔP_{max}) at 270.0 K was around 1.0 MPa for the last three runs (curves E–G), consistent with the heating-cooling experiments (Fig. 2). By fitting a simple linear equation to curve B (Fig. S2), it was extrapolated that the bulk H_2O–THF solution (no polyHIPE) would require >15000 min (>11 days) to reach 90% of the potential H_2 enclathration capacity, assuming $\Delta P_{max} = 1.0$ MPa. By contrast, 90% of ΔP_{max} was reached after only 60 min in the presence of the polyHIPE support, representing a >250-fold kinetic enhancement. Similar kinetic enhancements were observed at higher initial H_2 pressures (>13.8 MPa, Fig. S3). We also observed significant kinetic enhancements for semi-clathrate hydrates formed with tetra-n-butylammonium bromide (TBAB, Figs. S4–S6) with respect to comparable bulk, unmixed systems.[7]

These findings suggest a generic solution to recyclable gas charging in clathrate hydrates on a practicable timescale. The amount of H_2 stored is well below the practically useful level, as also found for bulk, unsupported systems.[5] However, preliminary experiments show similar kinetic enhancements (Figs. S7–S9) for methane hydrates,[9] which are perhaps closer to practical utilization,[12] although in this case the absence of THF in the system leads to significant problems with polymer wettability. It is likely that both kinetics and gas storage capacities can be improved significantly with second-generation supports, especially systems that do not contain THF where pore wettability in these polystyrene-based materials is very limited.[13] For example, we recently synthesized much more hydrophilic emulsion-templated polymers with higher pore volumes (19.1 $cm^3\,g^{-1}$) and even lower bulk density (0.033 g cm^{-3}).[14]

Experimental

Synthesis and Characterization of PolyHIPE Support: Full details of the procedure for preparing this polyHIPE material can be found elsewhere [10,11a]. Briefly, the organic phase (10 cm^3) comprised divinylbenzene (5 cm^3; DVB, Aldrich 80 vol %, m- and p-divinylbenzene, the remainder m- and p-ethylstyrene, purified by passing through a column of basic alumina to remove the inhibitor) and porogen(s) (5 cm^3; chlorobenzene, 2-chloroethylbenzene, 1:1 v/v [10], Aldrich). To this was added a surfactant, sorbitan monooleate (2 cm^3; Aldrich, Span 80, HLB = 4.3). The aqueous phase (90 cm^3) contained potassium persulfate (0.2 g, Aldrich) and calcium chloride (1.0 g, Aldrich). The separate organic and aqueous phases were purged with nitrogen for 15 min, and then the aqueous phase was added dropwise to the organic phase under nitrogen with constant mechanical stirring. The material was purified as described previously [10]. The morphology of the polyHIPE was observed using a Hitachi S-4800 cold field emission scanning electron microscopy (FE-SEM) instrument. The dry polymer samples were prepared on 15 mm Hitachi M4 aluminum stubs using either silver dag or an adhesive high-purity carbon spectro tab. The samples were then coated with a 2 nm layer of gold using an Emitech K550X automated sputter coater. The FE-SEM measurement scale bar was first calibrated using certified SIRA calibration standards. The BET surface area ($P/P_0 = 0.05$–0.20) was measured by nitrogen adsorption at 77.3 K using an ASAP2420 volumetric adsorption analyzer (Micromeritics). Samples were degassed at 90 °C for 15 h under vacuum before analysis. The pore size distribution analysis was conducted by mercury porosimetry. Bulk densities and macropore size distributions were recorded using an Autopore Mercury Porosimeter IV 9500 (Micromeritics) over a pressure range of 0.007–4000 bar. Intrusion volumes were calculated by subtracting the intrusion arising from mercury interpenetration between particles (pore size >150 µm) from the total intrusion.

Clathrate Hydrate Formation: A stock solution of tetrahydrofuran (5.56 mol % THF, Aldrich in deionized water; THF·17H_2O) was prepared [4a]. Similarly, a 2.56 mol % solution of tetra-n-butylammonium bromide (TBAB, Fisher) with a stoichiometric composition of TBAB·38H_2O was prepared, as described previously [7]. To carry out the gas uptake kinetic experiments, 20.0 g of the stock solution (either THF·17H_2O or TBAB·38H_2O) was loaded into a 60 cm^3 high-pressure stainless steel cell (New Ways of Analytics, Lörrach, Germany) together with the polyHIPE support (if used). For methane clathrate experiments, pure deionized water (20 g) was used. The temperature of the coolant in the circulator bath was controlled by a programmable thermal circulator (HAAKE Phoenix II P2, Thermo Electron Corporation). The temperature of the compositions in the high pressure cell was measured using a Type K Thermocouple (Cole-Parmer, −250–400 °C). The gas pressure was monitored using a high-accuracy gauge pressure transmitter (Cole-Parmer, 0–3000 psia). Both thermocouple and transmitter were connected to a Digital Universal Input Panel Meter (Cole-Parmer), which communicated with a computer. Prior to experiments, the cell was slowly purged with hydrogen (UHP 99.999%, BOC Gases, Manchester, UK) or methane (UHP 99.999%, BOC Gases, Manchester, UK) three times at atmospheric pressure to remove any air, and then pressurized to the desired pressure at the designated temperature. The temperature (T, K) and pressure (P, psia) and time (t, min) were automatically interval-logged using MeterView 3.0 software (Cole-Parmer). Using this set up it was possible to obtain high resolution data (for example, 2 seconds between individual [T, P, t] points, 90000 data points in a 1500 min experiment). The apparatus is shown schematically in Figure S1. Control experiments using 20.0 cm^3 of glass beads plus 3.0 g polyHIPE or 23.0 cm^3 of glass beads showed that the system did not leak: no pressure drop occurred over 1200 min (Fig. 2 in main paper and Figs. S3 and S5 in SI). Assuming the true density of the polyHIPE and clathrate hydrates to be approximately 1.0 g cm^{-3}, the free space volume of the cell (36.9 cm^3) was obtained by subtracting the sum volume of clathrate and support. This was confirmed independently by measuring the free volume with helium gas at 270.0 K. The hydrogen enclathration capacity was evaluated approximately using the ideal gas law, the pressure drop (ΔP), and the temperature. In addition, GASPAK v3.41 software (Horizon Technologies, USA) was employed to calculate the hydrogen enclathration capacity, taking into account non-ideality factors.

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