Supporting Information

Rapid and Reversible Hydrogen Storage in Clathrate Hydrates Using Emulsion-Templated Polymers

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Please note – referencing for Supp. Info. (pg. S11) is separate from main text

Experimental Section

Synthesis and characterization of polyHIPE support. Full details of the procedure for preparing this PolyHIPE material can be found elsewhere.[1] Briefly, the organic phase (10 cm³) was comprised of divinylbenzene (5 cm³; 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 cm³; chlorobenzene, 2-chloroethylbenzene, 1:1 vol/vol.[1a] Aldrich). To this was added a surfactant, sorbitan monooleate (2 cm³; Aldrich, Span 80, HLB = 4.3). The aqueous phase (90 cm³) 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.[1] The morphology of the polyHIPE was observed using a Hitachi S-4800 cold Field Emission Scanning Electron Microscope (FE-SEM). The dry polymer samples were prepared on 15 mm Hitachi M4 aluminium 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 Brunauer-Emmett-Teller (BET) surface area (P/P₀ = 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 0.10–60000 psia. 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•17H₂O) was prepared.[2,3] Similarly, a 2.56 mol. % solution of tetra-n-butylammonium bromide (TBAB, Fisher) with a stoichiometric composition of TBAB•38H₂O was prepared, as described previously[4]. To carry out the gas uptake kinetic experiments, 20.0 g of the stock solution (either THF•17H₂O or TBAB•38H₂O) was loaded into a 60-cm³ high pressure stainless steel cell (New Ways of Analytics, Lörach, 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 PressureTransmitter (Cole-Parmer, 0–3000 psia). Both thermocouple and transmitter were connected to a Digital Universal Input Panel Meter (Cole-Parmer), which communicates 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 \( (T, \text{K}) \) and pressure \((P, \text{psia})\) and time \((t, \text{min})\) 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, 90,000 data points in a 1500 min experiment). The apparatus is shown schematically in Fig. 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 Fig. 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 \((\Delta P)\), 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.

![Figure S1. Schematic diagram of the experimental apparatus.](image-url)
In the period 2000–4300 min
\[ P = 0.000519t + 11.31 \]

**Figure S2.** Kinetic plot of hydrogen enclathration in bulk THF-H₂O clathrate hydrate (no polyHIPE support) showing linear fit to applied to the data in the period 2000–4300 min after H₂ addition.

\( \Delta P_{\text{max}} = 178 \text{ psi} \)

**Figure S3.** Kinetic plots of hydrogen encapsulation in THF-H₂O clathrate hydrate at higher initial H₂ starting pressure at 270.0 K: (a) 23-cm³ glass beads (baseline); (b) THF-H₂O (20.0 g), no polyHIPE; (c) THF-H₂O (20.0 g) + activated carbon powder (10.0 g); (d) THF-H₂O (20.0 g) + polyHIPE (3.0 g). This data suggests that microporous activated carbon is ineffective in accelerating the kinetics, unlike the case of methane where the gas may also be physisorbed in wet carbons.[5] Other studies have shown that hydrogen enclathration capacity and occupancy are dependent on the hydrogen pressure.[6]
Table S1. Amount of H2 enclathrated in polyHIPE-supported THF-H2O clathrate, as measured by volumetric release experiments, as a function of venting temperature.

<table>
<thead>
<tr>
<th>Vent temperature (K)</th>
<th>H2 enclathration wt. % (based on THF-H2O)</th>
<th>Hydrogen encapsulation wt. % (+ polyHIPE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>270</td>
<td>0.11</td>
<td>0.09</td>
</tr>
<tr>
<td>270</td>
<td>0.15</td>
<td>0.13</td>
</tr>
<tr>
<td>198</td>
<td>0.33</td>
<td>0.28</td>
</tr>
<tr>
<td>198</td>
<td>0.41</td>
<td>0.35</td>
</tr>
<tr>
<td>77</td>
<td>0.48</td>
<td>0.41</td>
</tr>
<tr>
<td>77</td>
<td>0.53</td>
<td>0.47</td>
</tr>
<tr>
<td>&lt;130</td>
<td>0.4 to 0.5</td>
<td>/</td>
</tr>
</tbody>
</table>

*a wt. % H2, adjusted for system to take into account additional mass of the polyHIPE.

A series of volumetric release experiments was carried out to (a) confirm the H2 capacities calculated from the observed pressure drop in the reactor and; (b) to investigate the effect of temperature on enclathration capacity (for example, effects of limited clathrate stability upon venting at higher temperatures). For experiments where the reactor was vented at 270 K (the temperature of the kinetic experiments), the excess H2 was rapidly vented (in situ) and the vent valve closed as soon as atmospheric pressure was reached. Subsequent warming released the additional hydrogen, which was collected and measured by volumetric displacement. For lower temperatures the following procedure was used. After H2 enclathration was deemed to be complete, the cell was removed from the bath and quenched at the designated temperature: either 198 K (solid CO2) or 77.3 K (liquid nitrogen). Once the internal cell temperature was constant, the pressure was vented rapidly to atmospheric pressure (as above), the valve closed, and then the reactor warmed up to 293 K to measure the volume of hydrogen released during hydrate dissociation, as above. In all cases, measurements were calibrated to take account of gas expansion in the free space during warming (this was particularly important for the experiments at 77.3 K). The data is compiled in Table S1. It was found that venting at different temperatures significantly affected the amount of hydrogen evolved. At 77.3 K, the amount of H2 evolved was around 0.5 wt %, consistent with the values reported by Strobel et al.\textsuperscript{[3]} under similar $T$, $P$ conditions. It is likely that stabilization of the clathrate by cooling (in the absence of an over-pressure of H2) is important, as found in NMR studies where some H2 was lost with time even when the temperature was maintained at 175 K.\textsuperscript{[3]} It is also possible that additional H2 enclathration occurs during cooling, particularly since the capacities calculated from $\Delta P$ at 270 K are lower than 0.5 wt. % and much closer to the values calculated volumetrically at 270 K (first two entries in Table S1).
Figure S4. P-T plots of cooling and heating for H$_2$-TBAB-H$_2$O ternary system (semiclathrate hydrate) under hydrogen pressure (temperature ramp: 2.0 K/h): (A) without polyHIPE support; (B) with polyHIPE support (20.0 g TBAB-H$_2$O solution mixed with 3.4 g polyHIPE). This data is broadly consistent with published results.$^{[4]}$ The pressure drop ($\Delta P_1 = 0.16$ MPa) for the semi-clathrate hydrate without the polyHIPE support (A) is lower than that observed using the support (B, $\Delta P_2 = 0.23$ MPa). In general, these TBAB salt solutions appeared to wet the hydrophobic polyHIPE support less well than the THF-H$_2$O solutions, and hence a more hydrophilic material might be beneficial (see discussion, main text).

Figure S5. Kinetic plots for hydrogen enclathration in TBAB-H$_2$O semi-clathrate hydrate conducted at 273.2 K; (a) 23-cm$^3$ glass beads (baseline); (b) TBAB-H$_2$O solution (23.0 g) without polyHIPE; (c) TBAB-H$_2$O solution (20.0 g) with polyHIPE support (3.4 g) (1$^{\text{st}}$ run); (d) TBAB-H$_2$O solution (20.0 g) with polyHIPE support (3.4 g) (2$^{\text{nd}}$ run). Again, a significant kinetic enhancement is observed in the presence of the polyHIPE support.
Figure S6. $P$-$T$ plot of enclathration and subsequent dissociation for H$_2$-TBAB-H$_2$O ternary system under hydrogen pressure (20.0 g TBAB-H$_2$O solution, 3.4 g polyHIPE support): a$\rightarrow$b, enclathration at 273.2 K showing exotherm and pressure drop; b$\rightarrow$c$\rightarrow$d$\rightarrow$e, heating process with a temperature ramp of 4.0 K/h resulting in dissociation (commencing at point c).
Figure S7. Kinetic plots of CH$_4$ enclathration in H$_2$O clathrate hydrate at 271.0 K; Deionized H$_2$O (20.0 g) without support; (b) H$_2$O (20.0 g) plus polyHIPE (3.0 g). In the absence of the polyHIPE support (bulk water, no mixing), a very small pressure drop was observed after 1200 min (curve (a)). This is consistent with very slow methane enclathration kinetics for bulk water. These slow kinetics may be due, for example to the formation of a “skin” of clathrate hydrate at the gas-water interface, as observed in other studies where the growth rate for methane hydrates was found to be inversely proportional to the thickness of the hydrate layer.[7] By contrast, a relatively large and rapid pressure reduction was observed in the presence of the polyHIPE support (curve (b)). The methane enclathration capacity derived from the pressure drop in curve (b) at 271.0 K after 1200 min ($\Delta P = 2.0$ MPa) was estimated to be approximately 2.6 wt % CH$_4$ (37 v/v STP) based on the mass of water added using the ideal gas law, and around 3.4 wt % as calculated using GasPak v3.41 software, which takes account of the nonideality of the gas. These values are significantly lower than the maximum capacity for CH$_4$ clathrate systems (~180 v/v STP)[8], most likely due to incomplete formation of the H$_2$O-CH$_4$ clathrate hydrate. This may result from the very poor wettability of the hydrophobic polystyrene support with pure water (no THF was present in this case) and the existence of substantial bulk water which forms methane clathrate on a longer timescale (see curve (a)). It should be noted that physisorption on the polyHIPE support (BET SA = 230 m$^2$/g) may contribute to the CH$_4$ uptake at this ($T$, $P$), unlike the case of H$_2$ where one would expect the contribution of physisorption to be very small under these conditions.[9]
Figure S8. $P$-$T$ plot for enclathration and dissociation of the CH$_4$-H$_2$O system under CH$_4$ pressure with H$_2$O (20.0 g) plus polyHIPE support (3.0 g): a→b, enclathration conducted at 271.0 K (CH$_4$ addition temperature) with associated exotherm; b→c→d→e, heating process with a temperature ramp of 2.0 K/h, clathrate dissociation commences at point C.

Figure S9. $P$-$T$ plots for cooling and heating of CH$_4$-H$_2$O system under CH$_4$ pressure (temperature ramp: 2.0 K/h): (A) H$_2$O (20.0 g) without polyHIPE support; (B) H$_2$O (20.0 g) with polyHIPE support (3.0 g).
References (Supporting Information)