Communication

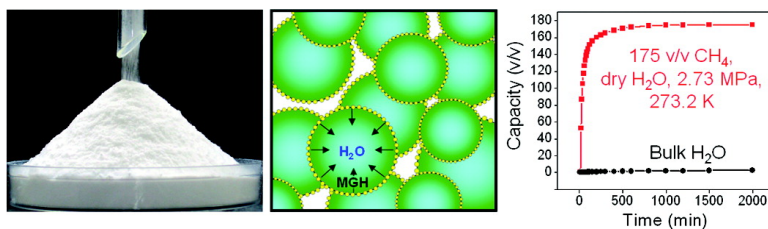# Methane Storage in Dry Water Gas Hydrates

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Methane Storage in Dry Water Gas Hydrates

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Gas hydrates, also known as clathrates, are nonstoichometric crystalline compounds composed of hydrogen bonded cages.[1−3] Natural gas hydrate (NGH) is an important natural energy source which also has potential for gas storage and transportation.[3] For example, one volume of methane gas hydrate (MGH) can yield approximately 180 v/v STP methane.[3] Liquefied NG has a much higher energy density but must be stored at very low temperatures (113 K). It has been suggested that it is economically feasible to transport NG in the hydrated form.[3] There are numerous practical problems, however, such as very slow clathrate formation rates and the presence of trapped, unreacted interstitial water in the hydrate mass. NGH is typically synthesized by cooling a mixture of NG and water under pressure or by the reaction of NG with preformed ice. The NGH formation reaction is an interfacial phenomenon, and rates of hydrate formation have been shown to be inversely proportional to the thickness of the hydrate zone and the surface area of the growing NGH particles.[4,5] Common methods for increasing clathrate formation kinetics—for example, the use of high pressures, vigorous mechanical mixing, surfactants, or micron-sized ground/sieved ice particles— can be achieved in the laboratory but may be less cost-effective and practical in real gas storage applications.

Previously, we used porous emulsion-templated polymers to increase the rate of hydrogen uptake in tetrahydrofuran-stabilized clathrates, but this approach was less successful with MGHs.[6] Dry water (DW) is a free-flowing powder prepared by mixing water, hydrophobic silica particles, and air at high speeds.[7] DW is a water-in-air inverse foam consisting of water droplets surrounded by a network of hydrophobic fumed silica which prevents droplet coalescence. Here, we report a means to greatly increase the rate of CH_4 uptake in MGH by forming the hydrate in preformed DW powders.

Figure 1 shows a typical sample of DW formed by rapid mixing of hydrophobic silica (H18), water, and air in a conventional blender. The particle size can be altered by varying the speed at which the mixing is carried out (Figure 1, lower; average primary droplet size <20 μm).

Figure 2 shows the cooling/heating curves for the CH_4−DW system with and without mixing. In an unmixed system (curve A; bulk water plus H18 silica), the $P-T$ relationship for CH_4 approximated to the ideal gas law during a continuous cooling/heating cycle. There was no evidence for substantial MGH formation or dissociation under these conditions (temperature ramp = 2.0 K/h; see Supporting Information, Figure S2). By contrast, MGH formation and subsequent dissociation occurred when particulate DW was employed (curve B), as shown by the dramatic pressure drop upon cooling and the rapid pressure rise upon heating, respectively.
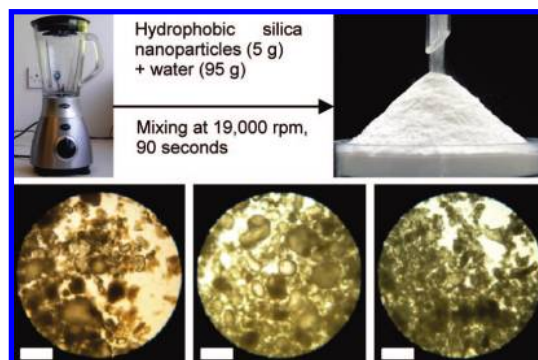
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Figure 1. Upper: Free-flowing DW powder prepared by aerating 5 g of hydrophobic silica nanoparticles H18 and 95 g of water at 19 000 rpm for 90 s. The powder is photographed flowing through a funnel. Lower: Optical micrographs showing three different batches of DW prepared at different mixing speeds (left to right: 16 450, 17 500 and 19 000 rpm). Scale bar = 50 μm in all cases.
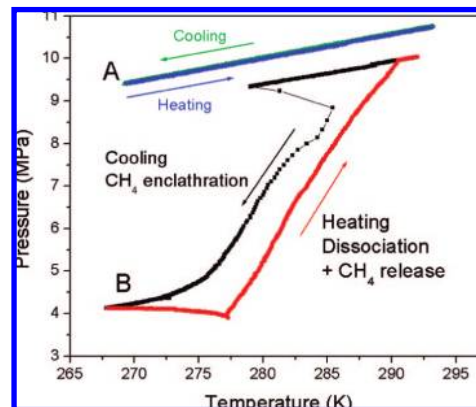

Figure 2. $P-T$ plots for CH_4 and DW during cooling and heating (temperature ramp: 2 K/h): (A) unblended mixture of water (19 g) and hydrophobic silica nanoparticles H18 (1 g); (B) 20 g DW powder (portion of a sample produced from 95 g of water + 5 g of hydrophobic silica nanoparticles H18) formed by mixing at 19 000 rpm for 90 s.

This behavior is similar to that reported recently for H_2 and CH_4 enclathration in polymer-supported hydrates[6] although the CH_4 uptake is much higher in this DW system (175 v/v versus approximately 37 v/v). MGH formation occurred when cooling to 279.0 K with an associated exotherm. During warming, MGH dissociation commenced at ∼277.5 K and was completed at ∼290.5 K. The formation of DW-MGH can be attributed to the highly dispersed water phase (Figure 1) which has a large surface area/volume ratio compared to the bulk water case.

Figure 3 shows kinetic plots for CH_4 enclathration in DW at 273.2 K (starting pressure = 8.6 MPa; see Figure S3). No mixing was applied in these gas uptake experiments. In all cases, the DW
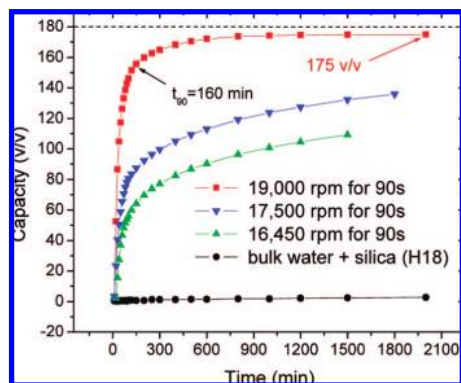
Figure 3. Methane uptake kinetics in DW-MGH at 273.2 K.

powders were formed by blending and then poured into an unmixed pressure vessel.

In the bulk water system with silica, only a very small pressure drop was observed even after 2000 min (see also Figure S3), and the gas capacity was very small (less than 3 v/v) over this time scale. These very slow kinetics are most likely due to the formation of an MGH "skin" at the gas−water interface.[8−10] By contrast, much faster methane enclathration was observed for the DW systems. The DW-MGH formation rate and saturation methane capacity were related to the size of the water droplets. The higher the mixing speed, the lower the average particle size (Figure 1). The DW prepared at the highest mixing speed (19 000 rpm) exhibited a saturation CH_4 uptake of 175 v(STP)/v at 273.2 K after 1500 min (t_{90}, the time to achieve 90% of this capacity, was about 160 min).[12] This CH_4 capacity is close to the maximum capacity for sI MGH assuming single occupancy of all cages (∼180 v/v at STP).[1,12,13] The effective storage pressure, that is, the CH_4 pressure at saturation uptake (Figure S3), was 2.73 MPa in this case. A short induction time was observed (typically 5−10 min) prior to DW-MGH formation.

Other studies show that MGH formation rates can be increased by stirring the mixture vigorously.[1−3,10] However, the energy required to stir the thickening slurry is significant. Similarly, crushed and sieved ice particles can be employed, but this is quite laborious and the material must be handled without melting. In our system, the gas−water interfacial surface area is increased by forming a dispersed water phase at ambient temperature prior to enclathration. The weight "penalty" is low because only 5 wt % silica is added with respect to water.

The kinetics of gas uptake were sensitive to relatively small changes in the speed of mixing in the DW formation (Figure 3). It is likely that enclathration rates could be increased further by the generation of smaller droplet sizes, although this could not be achieved using hydrophobic silica H18 and a standard domestic blender (Figure 1, upper).

The DW system can be reused after MGH dissociation, but the storage capacity and kinetics degrade significantly after a few cycles (Figures S4−S5). This stems from partial agglomeration of the water droplets which are destabilized by the freeze−warm process.[14] However, reblending the DW results in regeneration of the original enclathration kinetics (Figure S6). By contrast, the kinetic advantages of using crushed ice particles are entirely lost after one cycle if the water is allowed to melt.

The CH_4 storage capacities for these DW-MGHs come very close to U.S. Department of Energy targets[15] and compare favorably with high surface area physisorptive materials such as metal organic frameworks (MOFs),[16] activated carbons,[17] and microporous

organic polymers.[18] Our best storage capacity is lower than the leading value reported for an MOF (PCN-14) under comparable conditions (estimated 250 v/v excess CH_4 sorption at 270.0 K/2.7 MPa).[19] By contrast, MGHs are in principle stable for significant periods at atmospheric pressure with cooling,[20] something which is very hard to achieve with physisorptive materials.

In conclusion, DW gas hydrates could represent a viable platform for recyclable gas storage on a practicable time scale in a static, unmixed system. A number of challenges exist: for example, the further reduction of DW-MGH formation times, perhaps by more sophisticated blending. Another important advance would be to develop DW systems which are stable to multiple freeze−thaw cycles (Figures S4−S5). Perhaps most intriguing is the potential to use an additional guest molecule to stabilize the DW-MGHs at pressures much lower than the formation pressure,[21,22] although there are trade-offs here in terms of stability versus total gas storage capacity. Initial experiments involving tetrahydrofuran[21] or tetrabutylammonium bromide (TBAB)[22] failed because these guests destabilized the DW. Experiments are in progress to find a DW-MGH system which stores useful quantities of CH_4 at ambient pressure by identifying a compatible guest/nanoparticle combination. These results may also have broad significance in applications involving gas−liquid interfaces such as CO_2 sequestration, gas fractionation, and catalysis, particularly where continuous mixing is undesirable.

Supporting Information Available: Full experimental details, additional kinetic measurements, DW reuse tests, details of methane capacity calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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