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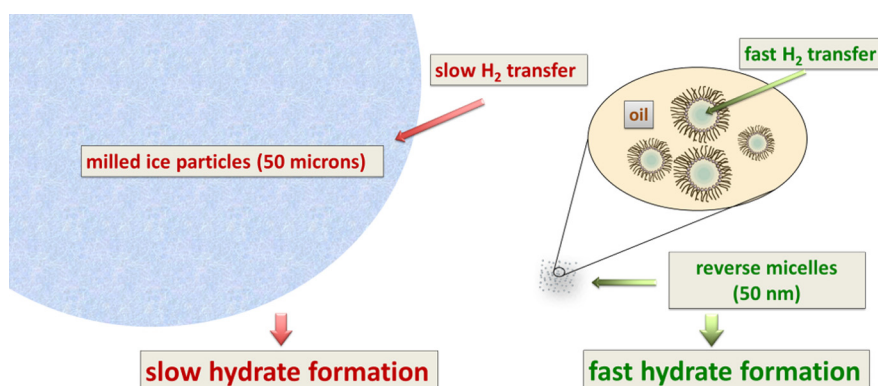
Reverse micelles enhance the formation of clathrate hydrates of hydrogen

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HIGHLIGHTS

- A reverse micelle process was used to enhance clathrate hydrates of hydrogen.
- Hydrogen was stored into clathrate up to 0.5 wt% at 10 MPa.
- Formation kinetics was in the order of minutes.
- Water-insoluble co-guests were effectively used with the reverse micelle.
- Enhancement of hydrate formation was due to a remarkable increase of surface-to-volume ratio of the water pseudo-phase.

GRAPHICAL ABSTRACT



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ABSTRACT

Hypothesis: Clathrate hydrates of hydrogen form at relatively low pressures (e.g., ca. 10 MPa) when a co-former compound is added. In that case, however, the gravimetric amount of stored hydrogen drops to less than 1 wt% from ca. 5.6 wt% without a co-former. Another factor hindering the entrapment of hydrogen into a clathrate matrix appears to be of a kinetic origin, in that the mass transfer of hydrogen into clathrates is limited by the macroscopic scale of the gas–water interfaces involved in their formation. Thus, the enhanced formation of binary (hydrogen + co-former) hydrates would represent a major achievement in the attempt to exploit those materials as a convenient means for storing hydrogen.

Experiments: Here, we present a simple process for the enhanced formation of binary hydrates of hydrogen and several co-formers, which is based on the use of reverse micelles for reducing the size of hydrate-forming gas–water interfaces down to tens of nanometers. This reduction of particle size allowed us to reduce the kinetic hindrance to hydrate formation.

Findings: The present process was able to (i) enhance the kinetics of the formation process; and (ii) assist clathrate formation when using water-insoluble cofomers (e.g., cyclopentane, tetrahydrothiophene).

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Abbreviations: CP, cyclopentane; DXL, dioxolane; DHF, 2,5-dihydrofuran; NG, natural gas; THF, tetrahydrofuran; THP, tetrahydropyran; THT, tetrahydrothiophene; W_0 , water/surfactant molar ratio; AOT, Bis(2-ethylhexyl) sulfosuccinate sodium salt; Nml, normal-milliliter (under Normal Conditions).

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1. Introduction

Hydrogen storage is one of the major issues hindering the development of the so-called *hydrogen economy*. To date, the main approaches for storing hydrogen are: (1) pressurization up to 70 MPa, (2) liquefaction at 20 K, (3) adsorption onto metal hydrides,

and (4) complexation to other inorganic and organic compounds, which methods all have drawbacks [1–4]. Storing hydrogen as a pressurized gas requires heavy-duty containers, and the pressures required to obtain an economically viable mass ratio are inherently hazardous [5], and the cost of composite materials for high-pressure containers is high [6]. Storing hydrogen as a liquid also poses safety and technological problems; further, a large fraction of the stored energy is lost when converting hydrogen gas to the liquid phase, and keeping it as a liquid under extreme temperatures (22 K). On the other hand, inorganic and organic supports (metals, intermetallic compounds, carbon nanotubes, etc.) can adsorb reversibly variable amounts of hydrogen at ambient temperature and pressure; however, desorption therefrom requires a high energy input and usually takes place at elevated temperatures [4,7].

Clathrate hydrates are ice-like compounds that form under low temperatures and high pressures. In hydrates, water molecules enclose small guests such as methane, carbon dioxide, tetrahydrofuran, hydrogen, etc., into a hydrogen-bonded, crystal network of Eulerian polyhedra [8]. Hydrates are studied, *inter alia*, because their plug oil and gas pipelines [9,10], and are being exploited as a potential means for gas mixture separation [11], and gas storage and transportation [12–14]. Main crystal structures for hydrates were determined by crystallographic methods, as structure I (sI), structure II (sII) and structure H (sH). A comprehensive review of crystallographic methods and hydrate structures is reported in the reference book by Sloan and Koh [8].

Since 1999, it has been known that hydrogen forms clathrate hydrates under very high pressure/low temperature [15,16]. In 2002, Mao et al. found that hydrogen hydrate crystallizes in structures labeled as structure-II (sII) clathrates [17,18]. The structure of the hydrogen clathrate was resolved by neutron diffraction as a function of pressure and temperature. The hydrogen occupancy in the clathrate was found to change proportionally to changes in pressure and/or temperature, while leaving the host structure virtually intact. Use of a co-former (e.g., THF) drastically reduces the equilibrium pressure of hydrogen hydrates [19], thus potentially opening the way to a clathrate hydrate-based technology for hydrogen storage [20–22]. THF turns out to be particularly suitable as a co-former, mainly due to its complete miscibility with water, while less water-soluble co-formers present inherent experimental difficulties due to the poor mass transfer in the water phase [23].

Strobel, Sloan et al. [24,25] and Peters and Sloan [26] recognized the need of increasing the gas-water exchange surface to increase hydrogen uptake. Notably, this was accomplished by using, *inter alia*, milled ice particles which were sieved down to ca. 50 μm in size. However, the milled ice/THF hydrate method of, e.g., Strobel et al. required previous formation of a solid THF hydrate at 250 K, then this solid hydrate was subjected to H_2 pressure to form the binary hydrate. Moreover, in some of Strobel's works [24], either long times (several hours to days) or higher pressures (15–40 MPa) were employed. Loskhin and Zhao [27] also described a method for hydrogen clathrate hydrate synthesis, in which ice and hydrogen gas are firstly supplied to a container at a first temperature and pressure, and then the container is pressurized with hydrogen gas to a second, higher pressure, where hydrogen clathrate hydrates are formed in the process. In those references, besides the inherent difficulties of enclosing hydrogen into clathrate cages, due to the small size and high fugacity of H_2 molecules, also the problem of an efficient mass transfer between the gaseous and the liquid and/or hydrate phases is acknowledged and discussed.

On the other hand, Irvin et al. [28] recognized that reverse micelles can be used to increase the surface area of gas-water contact in the formation of methane and carbon dioxide hydrates.

However, the authors did not suggest the use of reverse micelles for enhancing hydrogen hydrate formation, nor they recognized the role of the bulk organic solvent in the solubilization of poorly water-miscible molecules, e.g. a water-insoluble co-former. Methods are also known for the extraction of organic molecules from W/O microemulsions under hydrate forming conditions [29], and several papers were recently published on the combined use of W/O microemulsions and hydrates for the separation of gas mixtures [30–32], as a means for thermal energy storage [33], and W/O microemulsions in the form of ice slurries in crude oil as a model for NG hydrates for viscosity and yield stress studies [34]. Lee et al. [35] discussed the feasibility of obtaining high-content binary hydrates of THF and hydrogen, but their process takes weeks to complete.

In the present paper, we present a kinetically efficient method for preparing hydrogen hydrates, which is based on the formation of amphiphile-aided reverse micelles. The obtained micelles were macroscopically homogeneous, and the resulting water droplets could then be induced to form hydrate nanoparticles when the system was put under the appropriate P and T conditions. According to this method, binary co-former/hydrogen hydrates up to 0.5 wt% H_2 were obtained, with formation kinetics in the range of minutes. While this figure may seem quite low as compared to the current targets for hydrogen storage of 4.5 wt% (see, e.g., the U.S. Department of Energy website), it should be considered that hydrogen hydrates have the highest usable, specific energy content among known storage materials. Specifically, a 0.5 wt% H_2 in hydrate form corresponds to a usable energy content which is slightly higher than that provided by the same weight of H_2 pressurized at 200 bar [36].

The present method also allows for a broader choice of water-insoluble co-formers, with the bulk organic phase serving as a reservoir of the co-former which is kept ready for hydrate formation. On the other hand, the bulk dispersing phase may also act as a “partition buffer” with the aim of limiting the concentration of very water-soluble co-formers (e.g., THF) into the water droplets, thus potentially allowing to enhance the concentration of the hydrate former (e.g., H_2) in water. Furthermore, the reaction system can be kept under homogeneous conditions, thus avoiding clogging of the reactor due to agglomeration of hydrate particles. Indeed, hydrate nanocrystals which form from the water pools precipitate to the bottom of the reactor in form of a slurry which is free-flowing; this may be advantageous in case of a scale-up to a continuous production plant. The present process can be made continuous by simply replenishing water and co-former to the shrinking water pools, thus ideally leading to a continuous production of hydrogen hydrate.

2. Materials and methods

2.1. Materials

The structural and functional characteristics of a reverse micelle are extremely variable, and strongly dependent on the amphiphilic molecules used to stabilize their interfaces. A limited number of reverse micelle-forming molecules are known in the art, most of which refer to particular classes of anionics (AOT) or non ionics (Shell's NEODOLs, the Tweens, the Spans) amphiphiles [30,31]. We used a well known reverse micelle stabilizer (AOT from Sigma-Aldrich), with isooctane (Sigma-Aldrich, anhydrous 99.8%) as a bulk organic phase. H_2 was Alphasgaz 1, (Air Liquide); ultra-pure water (0.05 μS) was from a Millipore model Elix 3 ion-exchanger.

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