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Reversible methane storage in porous hydrogel supported clathrates

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HIGHLIGHTS

- Porous hydrogel microspheres were synthesised and mixed with dry-water, forming a colloidal system.
- Formation of methane gas hydrates in the colloidal system was fast, and high in hydration capacity.
- The system is reusable for methane storage.

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ABSTRACT

Methane gas hydrates are a promising alternative for storage and transport of natural gas. In this paper, porous poly(2-hydroxyethyl methacrylate) (PHEMA) and poly(2-hydroxyethyl methacrylate-co-methacrylic acid) (PHEMA-co-MAA) hydrogel microspheres were synthesised and examined for their application as a reusable scaffold for methane storage in their hydrated form. The hydration kinetics, methane storage capacity of the hydrogel microspheres, and a mixed colloidal system made of hydrogel particles and dry-water droplets were investigated in a 300 cm^3 steel vessel at 273.2 K and varying pressures. Hydration of methane in the mixed colloidal system is high in capacity and exceedingly reversible. Higher pressure and smaller size of hydrogel microspheres result in improved capacity and kinetics, however reduce the recyclability of hydration. The porous hydrogel particles alone are too soft for reuse and need to be improved for practical application.

1. Introduction

Gas hydrates are ice-like clathrate compounds consisting of a host lattice formed by hydrogen-bonded water molecules, with a large variety of small guest molecules enclosed in the lattice. They form when small gas molecules, including methane, carbon dioxide and hydrogen, come into contact with water at low temperature and high pressure (Sloan and Koh, 2008; Koh, 2002). It is generally accepted that the formation of gas hydrates is a gas–liquid or gas–solid interfacial phenomenon. The formation kinetics of gas hydrates is largely dependent on the nucleation and growth rate of the gas hydrates, the rate of methane transfer through the liquid or solid phase, and the rate of heat transfer.

Methane hydrates have a relatively high gas to solid ratio, storing up to 180 volume of gas (at standard conditions) in 1 volume of hydrate (Sloan, 2003) and can be held in a metastable solid state at atmospheric pressure (Stern et al., 2001). These properties make methane hydrates a promising alternative for storage and transport of natural gas (Gudmundsson and Graff, 2003; Mori, 2003; Masoudi and Tohidi, 2005). However, the application of the technology has been challenged by the slow formation rate and low storage capacity, as well as the thermal stability, of methane hydrates.

Common methods for increasing clathrate-forming kinetics include the use of high pressures, vigorous mechanical mixing, chemical additives and micron-sized ground ice particles (Sloan, 2003). Among the chemical additives, surfactants have been found to promote gas hydrate formation without affecting the thermodynamics of hydrate crystallisation (Zhong and Rogers, 2000; Yoslim et al., 2010; Okutani et al., 2008). Tetrahydrofuran (THF) (Giavarini et al., 2008), cyclopentane (Sun et al., 2003; Zhang et al., 2004), and tetra-*iso*-amylammonium bromide (TiAAB) (Wang et al., 2009) also have been used as hydrate promoters. The added promoter occupies some of the cavities in the clathrate structure, therefore reducing the volume available for the trapping of gas molecules (Carter et al., 2010). More recent work by Cooper's group has been focused on the use of high surface area polymers and dry-water. The latter is made of free-flowing water droplets surrounded by hydrophobic silica nanoparticles that prevent

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droplet coalescence (Binks and Murakami, 2006). For example, polystyrene-based polyHIPE (high internal phase emulsion) (Su et al., 2008), a foamed polyurethane (Talyzin, 2008) and a slightly cross-linked poly(acrylic acid) sodium salt (PSA) (Su et al., 2009) have been used to increase the storage capacity of hydrogen in THF-stabilized clathrates. However, using the same materials as a support media for methane storage was less successful. TiAAB semi-clathrates were used with PolyHIPE for reversible methane storage. Up to 20 charge-discharge cycles were accomplished. However, only 35–40 v/v storage capacity was achieved (Wang et al., 2009). The low methane storage capacity was assumed due to the hydrophobicity of the polymer and its poor water wettability. The use of dry-water by the same group achieved a much higher methane storage capacity (175 v/v) and a relatively rapid formation rate of methane hydrates (Wang et al., 2008). The authors expanded their work and utilised a gelling agent to form ‘dry gel’ so as to stabilise the dry system toward coalescence, therefore improving the recyclability of the material. One of the reported ‘dry gel’ systems was found to be recyclable over eight heating/cooling cycles with a gas capacity of 130 v/v (Carter et al., 2010). Inspired by the work of Cooper's group, we investigated the possibility of utilisation of cross-linked three dimensional porous poly(2-hydroxyethyl methacrylate) (PHEMA) hydrogel microspheres as support for methane hydrate formation.

PHEMA polymers are often produced by free radical polymerisation of hydroxyethyl methacrylate (HEMA) in the presence of a cross-linker and an initiator. When in contact with water, PHEMA polymers absorb and retain large amounts of water, becoming hydrogels. These hydrogels maintain a transparent and homogenous network that is suitable for such applications as contact lenses and intraocular lenses, for which optical clarity and limited diffusional characteristics are required. When PHEMA hydrogels are produced in the presence of porogens or a large amount of water, phase separation occurs as a consequence of thermodynamic interactions between water and the polymer network. This leads to the formation of a spongy and opaque hydrogel containing interconnected pores much greater than those in the homogenous hydrogels (Lou et al., 2004). These hydrogels have been found useful in the development of ophthalmic implants and controlled drug delivery systems (Chirila et al., 1998; Hicks et al., 2006; Lou et al., 2007; Wang et al., 2010). The high water content, excellent hydrophilicity and interconnected pores of these hydrogels could be ideal to support the methane hydrate formation and to enhance gas permeation and interactions with water molecules. In this work, porous microspheres of PHEMA and a copolymer of HEMA with methacrylic acid (MAA), PHEMA-co-MAA, were produced by suspension polymerisation in the presence of a porogenic mixture of cyclohexanol and 1-octanol (Horak et al., 1993). The produced porous PHEMA spherical hydrogels were examined, alone and together with dry-water, for reversible methane storage. The hydrate formation kinetics and capacity, and the reusability of these hydrogels were investigated.

2. Experimental

2.1. Materials

2-Hydroxyethyl methacrylate (HEMA) and ethyleneglycol dimethacrylate (EDMA) were supplied by Bimax. 2.2'-Azobis(2-methylpropionitrile) (AIBN) was purchased from Sigma-Aldrich and recrystallised from ethanol prior to use. Cyclohexanol (99%) was purchased from APS Chemicals. Other chemicals including 1-octanol (99%), poly(N-vinyl-2-pyrrolidone) (PVP, MW = 360,000), and methacrylic acid (MAA, 99%) were purchased from Sigma-Aldrich and used as received.

2.2. Preparation and characterisation of hydrogel microspheres

The following procedure was used to prepare the hydrogel microspheres: to 15 ml of porogen mixture (organic phase) containing 1-octanol and cyclohexanol of 2:3 volume ratio, 9.5 ml of monomer (HEMA or HEMA-MAA at a volume ratio of 8.5:1), 0.1 g of initiator (AIBN), and 0.5 ml of crosslinking agent (EDMA) were added and well mixed. The organic phase was then mixed with 75 ml of a 1% PVP aqueous solution in a glass flask, then purged with nitrogen for 30 min. The polymerisation was carried out at 70 °C for 8 h, with continuous stirring at 180 rpm. After cooling to room temperature, the polymer particles were washed with water, methanol and water, successively. The hydrogel particles were fractionated into two portions, $<100\ \mu$m and $>100\ \mu$m, using a Nylon 100 μm mesh (Safer Pty Ltd) and suspended in water for storage (Fig. 1a). Soft hydrogel particles (Fig. 1b), after the removal of free water from the suspension, were used for further investigation.

SEM images of hydrogel microspheres were taken on a Philips XL30. The necessary conductivity was guaranteed through a gold coating which was applied through physical vapour deposition (PVD). All hydrogel microspheres were freeze-dried prior to the SEM examination. Light microscopy images of the dried microspheres were obtained using a Nikon Optiphot-2 with a Pulnix digital camera. The ζ-potential of the microspheres was measured using a Malvern Zetasizer Nano-ZS and folded capillary cells (DTS 1060 from Malvern Instrument).

2.3. Preparation of mixed dry-water and hydrogel particles

Mixed dry-water and hydrogel particles were produced using the method reported by Carter et al. (2010). In brief: dried

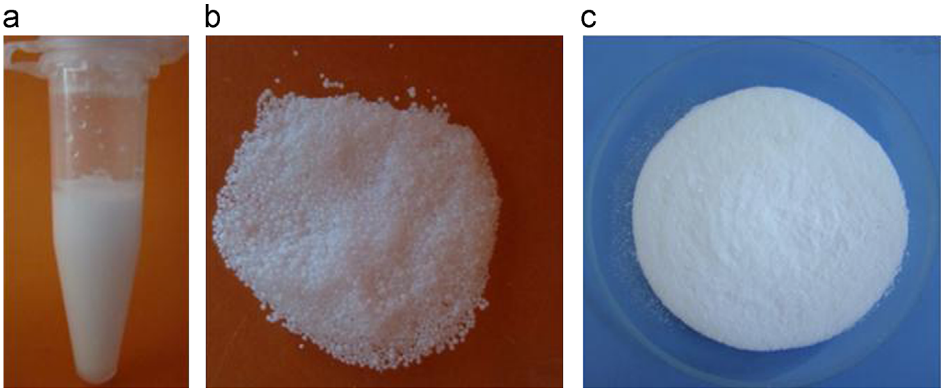

Fig. 1. Photographs of (a) water suspension of hydrogel particles, (b) free hydrogel particles, and (c) mixed hydrogel particles with dry-water.