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An investigation on repeated methane hydrates formation in porous hydrogel particles

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HIGHLIGHTS

- Porous hydrogels particles (HP) enhance reversible methane storage.
- High storage capacity requires high water contend in HP and suitable water-HP ratio.
- Stable porous structure and mild operation pressure improve the reversibility.

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ABSTRACT

Porous hydrogel particles of poly(2-hydroxyethyl methacrylate) (PHEMA) and poly(N-isopropylacrylamide) (PNIPAAm) with varying water absorbability and quantities were investigated upon their ability and stability to support the reversible methane hydrates storage in the presence of silica nanoparticles and water. Results from experimental and computational simulation indicated that the equilibrium water content and types of hydrogels, and the quantity of the hydrogel particles used in the mixture affect the hydrate formation kinetics. At the experimental condition of 4.5 MPa, all types of porous hydrogel particles were proved to be effective to store methane in the hydrates form. A storage capacity of 206 cm^3 methane gas (as at standard temperature and pressure) per gram water was achieved when the hydrate forming mixture contained four parts of PHEMA20, one part of silica nanoparticles and fifteen parts of water. Quantitative analysis using the shrinking-core model indicated that the presence of the hydrogel particles could increase the overall methane diffusivity and improve the hydrate formation kinetics, therefore the overall water conversion rate also enhanced. A strong reversibility was demonstrated by the added porous hydrogel particles. Changing water uptake by the hydrogel particles during the cool-thawing procedure was evident by the simulated water distribution data. The hydrogels with higher equilibrium water content, greater pore volumes and more stable porous structures and the lower operational pressure have shown better methane storage capacity and reversibility.

1. Introduction

The application of hydrate technology for methane and hydrogen storage and the carbon dioxide capture and separation, has attracted increasing attention in recent years [1–7]. Methane hydrates form at high pressure and low temperature with a solid crystalline structure that is made of hydrogen bonded water cages in each of which a methane molecule is encased [8,9]. Upon dissociation, one volume of solid methane hydrates can release 150–180 volumes methane gases at a standard temperature and pressure (STP) [10]. It is indicated that the energy density of methane hydrates is equivalent to a highly compressed natural gas (CNG), but slightly lower than liquefied natural gas (LNG) [10,11]. A study on gas transportation either through pipelines, or in the form of CNG, or LNG or hydrates [12], has demonstrated that the form of hydrates is a feasible and most cost effective option for the storage

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Nomenclature

AAD	absolute average deviation within experimental period, %
C	concentration of methane, mol/m^3
D_{f0}	initial methane diffusivity, m^2/s
K^*	methane adsorption rate constant, mol/(m^2·s·MPa)
M	molecular weight, g/mol
$n_{g,t}$	accumulated methane consumption at time *t*, mol
p	pressure, MPa
r	radius, m
R	gas constant, J/(mol·K)
t	time, s
T	temperature, K
V	volume, m^3
W_d	total gas molecule diffusion rate, mol/s
W_c	total gas consumption rate, mol/s
WC	water cut in different parts, %
z	the compressibility factor in real gas law

Greek symbols

β	hydration number
ζ	attenuation coefficient for methane diffusion
ρ	density, kg/m^3
φ	hydrates formation volume fraction

Subscript/superscript

0	initial point of time, at t = 0 s
DW	dry-water
eq	equilibrium
FW	free water
g	methane gas
H	hydrate
HP	hydrogel particles
i	inner radius of the hydrate shell
j	representation of the different systems with *j* = 0 for DW droplets, *j* = 1 for HP particles and *j* = 2 for FW droplets
o	outer radius of the hydrate shell
t	time
w	water

and transportation of stranded natural gases in the small scale, medium distance operations [1], due to the relatively large gas storage capacity of methane hydrates.

However, the large-scale application of methane hydrates has been hindered by a few practical problems [5], including the slow formation kinetics of gas hydrates [13]. Increasing hydrates formation rate might compromise the gas capacity, therefore reducing its effectiveness. The un-reacted interstitial water trapped between solid hydrates particles is also a problem, which occupies a large percentage of the total volume, therefore not only increases the maintenance cost but also decreases the gas storage capacity [14]. Many studies have been carried out to improve the kinetics rate by enhancing the mass and hear transfer during the hydrate formation process. Reported methods include the use of chemical additives such as gas hydrate promoters [15–19] and surfactants [14,15,20–35], enhanced mechanical mixing through stirring [32,36–38], spring [39–41] or injecting [42,43], bubbling [44] or foaming [45], the application of such porous media as active carbon [46–48], metal framework [49–52], hydrophilic polymer materials [53–56], and silica nanoparticles [57–60] or silica gels [61,62]. Several technical difficulties have been encountered when these approaches are employed. For instance, the effect of chemical additives changes with the type and initial concentration added to the aqueous phase [30]. The methods for improved mixing always require high energy consumption which is not cost effective [5]. The porous media is able to improve the mass transfer [46–62]. However, the stability and recyclability is of concerns [55–57,62]. Our previous study has shown that porous hydrogel particles could be used to enhance the hydrate formation rate [55]. Higher pressure and smaller hydrogel particle sizes resulted in improved the formation kinetics, however with reduced reversibility for the methane storage [55]. The value of ζ-potential of the investigated hydrogel particles showed little influence to the gas storage capacity and the hydrates formation kinetics.

The present work aims to study the methane storage capacity and the reversibility of porous hydrogels of varying water absorbability and porous structures. Porous particles of poly (2-hydroxyethyl methacrylate) (PHEMA) and poly (N-isopropylacrylamide) (PNIPAAm) were synthesized and mixed with silica nanoparticles and water for the investigation. The mixture consisted of hydrogels particles and dry water (water droplets encased by hydrophobic silica nanoparticles). The latter has been reportedly effective, however insufficiently stable in the reversible storage of methane in the form of hydrates [57]. The experimental results from the current work have demonstrated that the equilibrium water content (EWC), the porous structure and the quantity of the hydrogel particles used have a strong impact on the hydration kinetics. In order to understand how these parameters have affected the performance of the particles, computational simulation was applied to the experimentally obtained methane storage data, using a modified shrinking core model [56]. The computed diffusion and kinetic parameters indicated that the presence of hydrogel particles increased the methane diffusion in general. The unabsorbed or encased water in the mixed hydrogel-dry water system has a negative impact on the hydrates formation kinetics and storage capacity. The findings of this work provide an insight into the behavior of hydrogels as a support to the formation of methane clathrates, which is an on-going research topic in the field of methane storage and transportation.

2. Materials and methods

2.1. Materials

Porous hydrogels of PHEMA and PNIPAAm were synthesized according to our previously reported method [63–66] in which water was used as a solvent in the polymerization in order to generate phase-separated porous structure as shown in Fig. 1. The hydrogels used for this study included PHEMA10, PHEMA20 and PNIPAAm20 in which, *10* and *20*, indicate the percentage of water used in the polymerisation mixture. The produced hydrogels were first freeze dried using a DYNAVAC freeze drier (Model FD3) and then put into a blender to be crashed into powders, which are further mixed with silica nanoparticles HB630 (Guangzhou GBS High-Tech & Industry Co., Ltd) to produce the mixed dry-water/hydrogel particle systems (DW-HP) (Fig. 1 Right) for the methane hydrates formation. The method to produce the DW-HP can be found in the previous work [55]. The mass ratio of HB and HP and water (WA) was 1:4:15 and 1:2:17 respectively for different mixtures