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Multiple adsorption resistance model for constituent molecular effects in hydrogen clathration kinetics in clathrate hydrate particles

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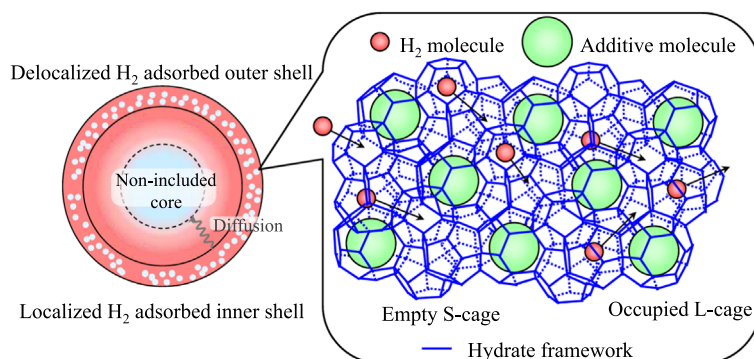
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HIGHLIGHTS

- Properties reported on clathrate hydrates with guest additives for H₂ storage.
- Guest additives: THF, THF-d8, furan, cyclopentane and tetrahydrothiophene.
- Three resistance model: hydrate framework, guest inclusion cage, and H₂ adsorbed shell.
- Non-included guest additives affect H₂ diffusion pathway.
- S-cage distortion affects H₂ adsorption rate.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption rates are reported for H₂-tetrahydrofuran (THF), H₂-THF (D₂O), H₂-THF-d8, H₂-furan, H₂-cyclopentane (CP) and H₂-tetrahydrothiophene (THT) binary clathrate hydrates at temperatures of 265–273 K and pressures of 4–10 MPa. Adsorption rates of H₂-furan and H₂-6.8 mol% THF binary clathrate hydrates were the fastest among these binary clathrate hydrates. The lattice constant of hydrates were determined to analyze the adsorption data with a newly proposed multiple adsorption resistance (MAR) model. The effect of the non-included additive molecule on hydrogen adsorption rate was important because they promoted formation of pores and grain boundaries when hydrate particles formed. Activation energies, ΔE_{D_s} , for H₂ diffusion into clathrate hydrates calculated from the Arrhenius plots depended on the hydrate guest additive and were determined to be: 18.0 kJ/mol (6.2 mol% THF), 30.7 kJ/mol (5.6 mol% THF), and 100 kJ/mol (cyclopentane). Based on the ΔE_{D_s} values, H₂ diffusion pathway in hydrate particles depends on the clathrate hydrate formation process and the interactions between guest additive molecule and the host molecule.

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1. Introduction

Clathrate hydrates are crystalline compounds formed from host water molecules and one or more guest molecules. Both the

stability and structure of the gas clathrate hydrates depend on the type of guest molecule in the cavity of the occupied cages. Hydrogen clathrate hydrates form structure II at high pressures (≈ 200 MPa) (Mao et al., 2002) because molecular size of hydrogen is very small. Organic liquids such as tetrahydrofuran (THF) stabilize the structure of the clathrate hydrate above 273 K at atmospheric pressure (Florusse et al., 2004).

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The amount of hydrogen that can be stored in 5.6 mol% THF clathrate hydrate is lower than 1.05 wt% at 270–278 K (temperature cycled method) and 60 MPa (Strobel et al., 2006), at 277 K and 200 MPa (Ogata et al., 2008) for occupancy of hydrogen in all larger hexakaidecahedral ($5^{12}6^4$) cavities (L-cage) with THF molecules. In H_2 -0.6 mol% THF or acetone binary clathrate hydrates formed from ice particles, hydrogen storage can be increased to ca. 3.5 wt% at 255 K and 74 MPa due to occupancy of L-cages with 4 hydrogen molecules (Sugahara et al., 2010). Clathrate hydrate has characteristics such as complete recovery of H_2 without using high temperature (Florusse et al., 2004) so that the H_2 +guest additive molecule binary clathrate hydrate can be anticipated as a hydrogen storage material. Other potential applications for clathrate hydrates are as buffer or membrane materials.

Phase equilibria and hydrogen adsorption rates of the clathrate hydrates are important for their practical use. The hydrogen adsorption mechanism in hydrate particles is needed for improving H_2 storage amounts, improving H_2 storage rate through analysis of hydrogen clathrate hydrates under dynamic conditions.

Phase equilibria of some proposed guest additive molecules for structure II that have been reported are THF (Cruz Duarte et al., 2008; Florusse et al., 2004; Komatsu et al., 2010; Peters, 2009), cyclopentane (CP) (Du et al., 2010; Komatsu et al., 2010; Peters, 2009), tetrahydrothiophene (THT) (Tsuda et al., 2009) and furan (Tsuda et al., 2009). Phase equilibrium P - T boundaries of H_2 +furan and H_2 +THT hydrates are lower in temperature than those of H_2 +THF hydrate. The H_2 +CP binary clathrate hydrate is considered to exist at higher temperatures than THF, furan and THT clathrate hydrates. Thermodynamic stability is one of the issues in considering hydrogen occupancy and mobility of H_2O molecules in clathrate hydrates.

Phase equilibria of the clathrate hydrates are affected not only by the guest additive molecule but also by the host molecule. The phase boundary of H_2 +THF binary clathrate hydrate (D_2O) exists at higher temperatures than H_2 +THF binary clathrate hydrate (Peters, 2009). However, the deuteration effect is not observed when THF- d_8 is used as guest additive molecule (Peters, 2009). Hydrogen storage amounts have been studied with theoretical and experimental methods (Papadimitriou et al., 2009; Strobel et al., 2009), where it has been found that a relationship exists between the phase equilibria and the lattice distortion with the guest molecule (Martin and Peters, 2009). In considering the constituent molecular effects for practical use, not only phase equilibria, but also formation kinetics are important.

There has been considerable research on hydrogen clathrate hydrate formation kinetics (Hashimoto et al., 2012; Nagai et al., 2008; Ogata et al., 2008; Okuchi et al., 2007; Yoshioka et al., 2011) and dissociation kinetics (Ogata et al., 2008; Yoshioka et al., 2011) of H_2 -THF binary clathrate hydrate with hydrate particles. The occupancies in both formation and decomposition have very similar trends according to repeated cycles (Yoshioka et al., 2011). Hydrogen adsorption in THF clathrate hydrate particles has been analyzed by hydrogen delocalization model (Nagai et al., 2008) based on Kawamura et al. model (Kawamura et al., 2002) or the models including two steps based on the shrinking core model (Hashimoto et al., 2012; Nagai et al., 2008; Yoshioka et al., 2011). In H_2 -THF clathrate hydrate formation process, a model based on the shrinking core model could reproduce the experimental data closer than the delocalization model (Nagai et al., 2008). Although formation kinetics have been reported for furan and THT, hydrogen diffusion behavior in furan and THT clathrate hydrate particles is different from that in THF clathrate hydrate particles (Tsuda et al., 2009), and these have not been analyzed with kinetic models yet. Moreover, little information is known about the stability of clathrate hydrates such as H_2 +CP clathrate hydrate and H_2 +THF clathrate hydrate (D_2O). The lattice distortion with

the guest molecules might affect hydrogen diffusion in the hydrate layer judging from the phase equilibria.

In this work, our objectives were to analyze the effect of host molecules (H_2O , D_2O) and guest additive molecules (THF, THF- d_8 , furan, CP, THT) on hydrogen adsorption behavior in clathrate hydrates. New formation data are reported for these host and guest additive combinations. For hydrophobic guest additive molecules (furan, CP, THT), the ratio of the hydrate and ice was estimated by 1H NMR. These formation data are quantitatively analyzed with a previous model (Hashimoto et al., 2012; Nagai et al., 2008; Yoshioka et al., 2011) and a newly proposed model. The new kinetic model is constructed on the assumption that the formation of H_2 +guest additive clathrate hydrate from a particle occurs along three boundaries which have different adsorption resistances. To study the dominant factors in the formation rate and adsorption mechanism, the results are analyzed with these models and discussed. Hydrate particles are characterized with powder X-ray diffraction (XRD) so that the parameters in the kinetic model can be related to the hydrate cage sizes.

2. Experimental

2.1. Materials

Distilled and deionized water was used that had an electrical conductivity of 5.5 $\mu S/m$. H_2 gas (99.99%, Iwaki Suiso), tetrahydrofuran without stabilizer (99.5%, Wako Pure Chemical, Inc.), D_2O (Deuterated rate: 99.8%, Kanto Chemical), tetradrofuran- d_8 (Deuterated rate: 99.5%, Kanto Chemical), cyclopentane ($\geq 99\%$, Aldrich), furan with stabilizer (BHT) ($\geq 99\%$, Tokyo Chemical Industry), tetrahydrothiophene ($\geq 99\%$, Tokyo Chemical Industry), and acetone- d_6 (Deuterated rate: 99.9%, Merck) were used without further purification.

2.2. Hydrate preparation

Batches of clathrate hydrate particles were made by loading water (or D_2O) and THF (or THF- d_8 , CP, furan, THT) into a perfluoroalkoxyethylene vessel in such a way that the concentration of organic liquids were 5.56 mol% with the contents being weighed to a precision of 1 mg with a balance (Mettler Toledo AX504) that was followed by cooling of the solution to 274 K with low temperature-controlled bath while stirring. The formed clathrate hydrates were cooled to 253 K in a freezer for at least 6 h. The solids were crushed with a mortar and pestle at liquid nitrogen temperatures and graded with stainless steel-type 316 sieves while being kept in the freezer at 253 K. Particle size ranges of 500–600 μm were used in the experiments. The formation of clathrate hydrates were confirmed with laser Raman spectrometer (JASCO, NR-2000), with a holographic grating, CCD (Princeton Instruments, Inc.) at room temperature and atmospheric pressure (Fig. S1). The existence of ice in clathrate hydrate particles was determined with XRD (Rigaku, type Ultima III) using the CuK α radiation (40 kV, 40 mA) at 123 K, and the lattice constant of the clathrate hydrate was calculated with RIETAN-2000 program. The proportion of ice to hydrate was estimated with 1H NMR (AV-400, Bruker BioSpin K.K.).

2.3. Experimental apparatus

Fig. 1 shows a schematic diagram of the experimental apparatus that was modified from the previous work (Komatsu et al., 2013). The reservoir tank system was designed to be separated from the equilibrium cell during the loading of the reservoir tank with H_2 . In the hydrate formation cell, the window was held externally with a O-ring (IIR-70°, Morisei Kako Co.) and the inner cell was made of

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