Applied Energy 228 (2018) 229–239

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Structural transition induced by cage-dependent guest exchange in $CH_4 + C_3H_8$ hydrates with CO_2 injection for energy recovery and CO_2 sequestration

Yohan Lee[a], Wonjung Choi[a], Young-ju Seo[b], Joo Yong Lee[b], Jaehyoung Lee[b], Yongwon Seo[a,*]

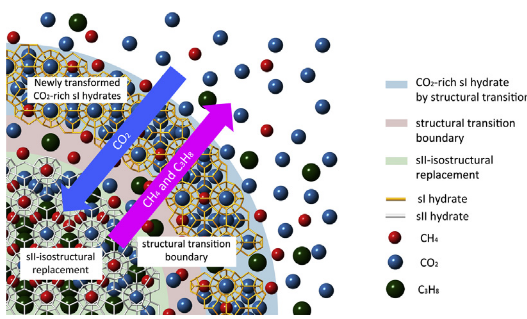
[a] School of Urban and Environmental Engineering, Ulsan National Institute of Science and Technology, Ulsan 689-798, Republic of Korea

[b] Petroleum and Marine Research Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon 34132, Republic of Korea

HIGHLIGHTS

- The guest exchange behavior during replacement was quantitatively investigated.
- The CO_2 occupation induced the depletion of C_3H_8 in the large $5^{12}6^4$ cages of sII.
- The partial structural transition occurred in the $CH_4 + C_3H_8$ - CO_2 replacement.
- The replacement was more significant at higher pressure of injected CO_2.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Gas hydrate
Replacement
CO_2 sequestration
Structure II
Strucutral transition

ABSTRACT

This study investigated a structural transition induced by cage-dependent guest exchange in the $CH_4 + C_3H_8$ hydrate with CO_2 injection for CH_4 recovery and CO_2 sequestration. The influence of the CO_2 replacement on the crystalline structure of initial $CH_4 + C_3H_8$ hydrates and the cage-dependent distribution of guest molecules were quantitatively investigated using powder X-ray diffraction, ^{13}C nuclear magnetic resonance spectroscopy, and gas chromatography. The quantitative analyses demonstrated that the CO_2 occupation caused the depletion of C_3H_8 molecules in the large $5^{12}6^4$ cages of structure II hydrates, thereby resulting in the subsequent transformation into CO_2-rich sI hydrates and the coexistence of structure I and structure II hydrates after the replacement. The guest-exchange behavior observed from time-dependent Raman spectra indicated that the replacement rate was increased with an increase in pressure of injected CO_2 and that the extent of the replacement was enhanced at higher pressure of injected CO_2. Overall experimental evidence of the partial structural-transition replacement suggests that CO_2 molecules first occupied structure II hydrates predominantly with the rapid guest exchange at the surface and that the initial structure II hydrates were subsequently converted to the CO_2-rich structure I hydrates from the surface to the inner side. Precise identification of the mechanism responsible for the partial structural transition occurring in the $CH_4 + C_3H_8$ - CO_2 replacement will be very helpful in developing a strategy for actual CO_2 injection into structure II gas hydrate reservoirs for energy recovery and CO_2 sequestration.

* Corresponding author.
E-mail address: ywseo@unist.ac.kr (Y. Seo).

https://doi.org/10.1016/j.apenergy.2018.06.088
Received 19 February 2018; Received in revised form 16 May 2018; Accepted 17 June 2018

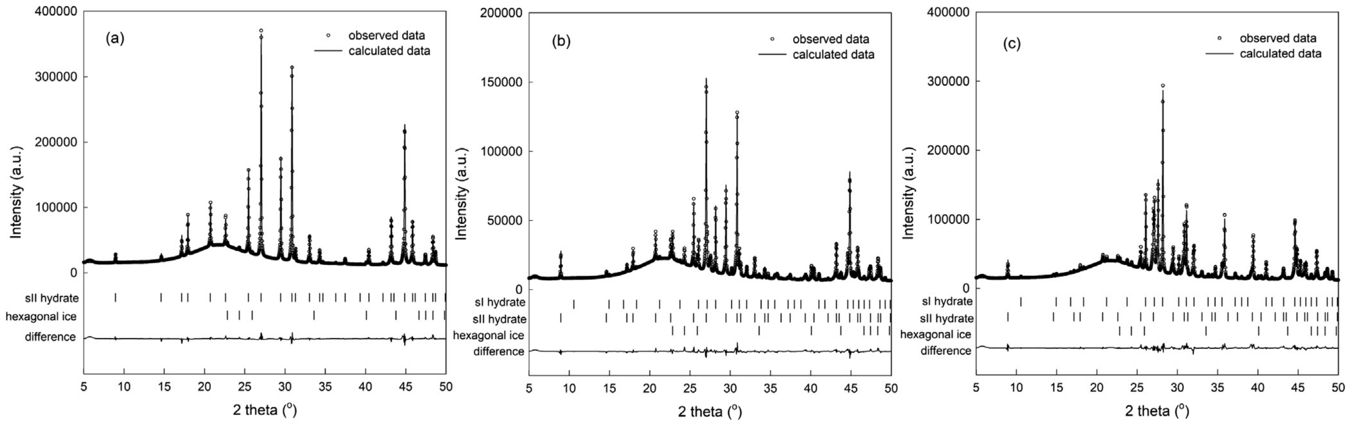


Fig. 1. PXRD patterns of (a) the initial CH_4 + C_3H_8 hydrate, (b) the hydrate replaced at 2.4 MPa of P_{CO2}, and (c) the hydrate replaced at 3.9 MPa of P_{CO2}. The vertical tick marks represent the calculated positions of diffraction peaks for sI, sII hydrates, and hexagonal ice.

Table 1
Crystallographic information regarding initial CH_4 + C_3H_8 hydrate and hydrates replaced at 2.4 and 3.9 MPa of P_{CO2}.

		Initial CH_4 + C_3H_8 hydrate	Replaced hydrate at 2.4 MPa of P_{CO2}	Replaced hydrate at 3.9 MPa of P_{CO2}
Structure		sII, cubic$Fd\bar{3}m$	sI, cubic $Pm\bar{3}n$ sII, cubic $Fd\bar{3}m$	sI, cubic $Pm\bar{3}n$ sII, cubic $Fd\bar{3}m$
Lattice parameter		a = 17.1337(5) Å (sII)	a = 11.8384(2) Å (sI) a = 17.1336(1) Å (sII)	a = 11.8394(6) Å (sI) a = 17.1341(9) Å (sII)
Phase ratio*	sI	–	15.7 ± 0.8%	64.2 ± 2.0%
	sII	99.5 ± 2.5%	79.9 ± 2.0%	34.9 ± 1.5%
	Ice	0.5 ± 0.1%	4.4 ± 0.1%	0.9 ± 0.1%
R_{wp}		9.0%	12.4%	13.1%

* The phase ratio was determined on the basis of the ratio of water molecules in each phase.

1. Introduction

Gas hydrates, also referred to as clathrate hydrates, are host-guest compounds that stabilize under specific temperature and pressure conditions with the occupation of proper-sized guest molecules in host cages made up of hydrogen-bonded water molecules [1]. In particular, various biogenic and thermogenic hydrocarbons are entrapped in natural gas hydrates (NGHs), which are found in deep-ocean sediments of continental margins or underneath permafrost regions in the form of three distinct structures. NGHs predominantly occur in the form of structure I (sI), which consists of pentagonal dodecahedron (5^{12}) and tetrakaidecahedron ($5^{12}6^2$) cages and primarily originates from biogenic gases heavily weighted to methane (CH_4). NGHs in the form of structure II (sII), which is composed of pentagonal dodecahedron (5^{12}) and hexakaidecahedron ($5^{12}6^4$) cages, generally contain other larger hydrocarbons, such as C_2H_6, C_3H_8, and C_4H_{10}, together with CH_4. It has recently been revealed that NGHs in the form of structure H (sH), which consists of pentagonal dodecahedron (5^{12}), irregular dodecahedron ($4^35^66^3$), and icosahedron ($5^{12}6^8$) cages, also occur in the gas hydrate reservoirs with thermogenic gases that contain much larger hydrocarbons, such as methylcyclopentane and neohexane [2,3].

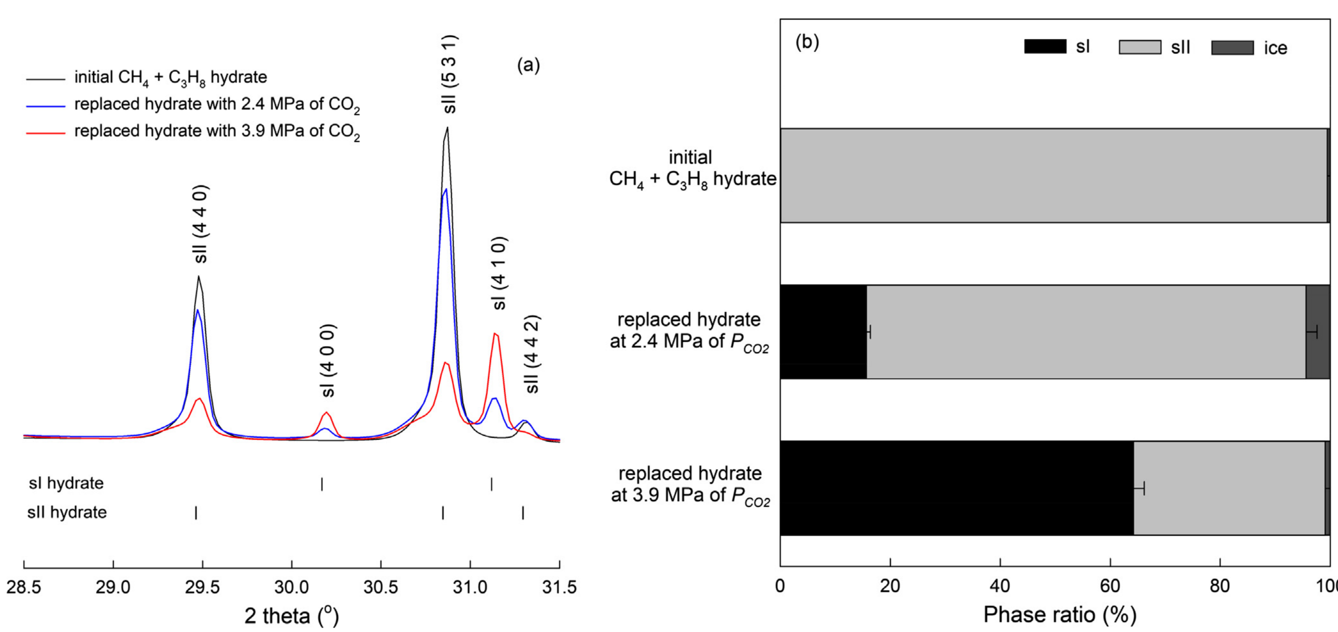


Fig. 2. (a) PXRD profiles of the hydrates replaced in the 2θ range of 28.5–31.5°, and (b) phase ratio of initial CH_4 + C_3H_8 hydrate, and hydrates replaced at 2.4 and 3.9 MPa of P_{CO2}.