

^{13}C NMR analysis of $\text{C}_2\text{H}_6+\text{C}_2\text{H}_4+\text{THF}$ mixed hydrate for an application to separation of C_2H_4 and C_2H_6

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Abstract—Mixed hydrates ($\text{C}_2\text{H}_4+5.56\text{ mol\% THF}$, and $\text{C}_2\text{H}_4+\text{C}_2\text{H}_6+5.56\text{ mol\% THF}$) were analyzed using ^{13}C MAS NMR spectroscopy. The hydrates were formed using a variety of feed gas compositions (100% C_2H_4 ; 20% $\text{C}_2\text{H}_4+80\%$ C_2H_6 ; 40% $\text{C}_2\text{H}_4+60\%$ C_2H_6 ; 60% $\text{C}_2\text{H}_4+40\%$ C_2H_6 ; and 80% $\text{C}_2\text{H}_4+20\%$ C_2H_6). According to the peak identification results, C_2H_4 molecules can occupy both the small and large cavities in the sI and sII hydrate structures, while C_2H_6 molecules can occupy only the large cavities of sI. Moreover, the mole fraction of C_2H_4 in the hydrate matrix was found to increase with increasing feed ratio of C_2H_4 . On the basis of the NMR analysis, a hydrate-based process for separating C_2H_4 and C_2H_6 by repeated hydrate formation and dissociation was proposed. For cases with a feed-gas mixture with 20% C_2H_4 and 80% C_2H_6 , a recovery of more than 88% C_2H_4 in the gas mixture could be achieved after five cycles of hydrate-based separation.

Keywords: Clathrate Hydrate, Ethane, Ethylene, Tetrahydrofuran, Separation, ^{13}C NMR

INTRODUCTION

Clathrate hydrates, known as gas hydrates, are crystalline materials formed by a physical combination of guest molecules and water-cage molecules that form at low temperature and high pressure. On a molecular scale, guest molecules are captured by hydrogen-bonded water cages in non-stoichiometric hydrates. In these hydrate structures guest-molecule repulsions open different sizes of water cages, forming three well-defined unit crystals that include cubic structure I (sI), cubic structure II (sII), and hexagonal structure H (sH) [1]. In recent years, clathrate hydrates have been studied for application in broad areas of energy and environment. These include applications such as methane gas recovery (from natural gas-hydrate deposits) and transportation [1]; carbon dioxide sequestration or substitution for the gases within natural hydrates in marine sediments [2]; and hydrogen storage [3]. The development of environmentally friendly gas separation processes using clathrate hydrates has been actively studied [4-6]. For a long time, extractive distillation, physical adsorption, chemical adsorption, and membrane processes for the separation of light olefins and paraffins have been studied in the petrochemical industry for replacement of traditional low-temperature distillation [7]. However, there is not a

commercialized process yet, and some studies of clathrate compounds have focused on their use as an alternative to high energy-consuming refrigerant distillation [8-10].

There have been numerous phase-equilibrium studies performed for pure as well as for mixed hydrates. In particular, the phase equilibria of hydrocarbons with one or two carbon atoms, which are widely encountered in petroleum and natural gas processing, have been intensively investigated [11,12]. Kang and Lee [10] investigated hydrate-phase equilibria of binary ($\text{CH}_4+\text{C}_2\text{H}_4$) hydrates and those of binary ($\text{C}_2\text{H}_6+\text{C}_2\text{H}_4$) hydrates. They also studied the cage occupancy distribution using microscopic analysis via solid-state ^{13}C NMR spectra of hydrate samples. Sun et al. [13] and Zhang et al. [14] reported on the hydrate phase equilibria and structure of methane+ethane and methane+ethylene hydrates in the presence of tetrahydrofuran (THF), known as a hydrate promoter. Ethane and ethylene are known guest molecules that form sI hydrates, and they are able to occupy only the larger cavities due to their molecular size. Alternatively, THF is a known guest molecule that forms sII hydrate. From the phase equilibria data of ethane, ethylene, and THF hydrate, it is believed that THF behaves as an inhibitor prohibiting the formation of sI hydrate, when ethane or ethylene mixed hydrates form with THF.

In this study, Solid phase compositions of binary hydrate samples prepared with 5.56 mol% THF and $\text{C}_2\text{H}_4+\text{C}_2\text{H}_6$ gas mixtures with various compositions were investigated using NMR spectroscopy and the new concept hydrate-based process for C_2H_4 and C_2H_6 separation was suggested on the basis of the spectroscopic data obtained. When mixed gas of various compositions of ethane and eth-

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*This article is dedicated to Prof. Huen Lee on the occasion of his retirement from KAIST.

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ylene was fed into THF hydrate, guest enclathration of the mixed gas reflecting the various compositions was observed in the THF hydrate via ^{13}C solid-state NMR spectroscopy. In addition, the mixed hydrate structure and the guest-molecule distribution in the small and large cavities of the hydrate were investigated using NMR-peak identification and quantitative analysis of ethane and ethylene molecules in THF hydrate lattices. The experimental and analytical results obtained in this study could provide fundamental data useful for designing hydrate-based processes able to alter conventional highly energy-consuming refining distillation in the petrochemical industry.

EXPERIMENTAL SECTION

Pure C_2H_4 and C_2H_6 , as well as gas mixtures at various concentrations, were supplied by Daemyoung Special Gas Co. (Korea). The pure C_2H_4 and C_2H_6 gases had nominal purities of 99.5 mol%. Gas mixtures of ($\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$) with concentrations referred to as 20, 40, 60, and 80 mol% C_2H_4 had nominal concentrations of 20.0, 40.0, 60.0, and 80.0 mol% C_2H_4 , respectively. Pure tetrahydrofuran (THF) with a minimum purity of 99.9 mol%, was supplied by Sigma-Aldrich Chemicals Co. These gases and liquid were used with high-performance-liquid-chromatography-(HPLC-) grade water, supplied by Sigma-Aldrich with a nominal purity of 99.99 mol%, to form clathrate hydrates. All of the materials were used without further purification or treatment.

Frozen 5.56 mol% THF and water solutions were stored in a refrigerator at 243 K for at least one day, and then ground to a fine powder ($\sim 200\ \mu\text{m}$). The powdered solid was exposed to C_2H_4 , C_2H_6 , and gas mixtures (30 bar) in a stainless steel (SUS) pressure cell that was already cooled. The C_2H_4 , C_2H_6 , and gas mixtures in the pressurized cell were kept at a temperature of 268 K for five days to induce hydrate formation. After the hydrate reaction (pressure drop due to the hydrate formation) reached the steady-state, the residual

gas was vented from the hydrate cell. The hydrate thus prepared, was packed into a 4-mm-o.d. zirconium rotor, cooled in liquid nitrogen for ^{13}C NMR analysis. For structural and microscopic studies, a 400 MHz Avance II+ Bruker Solid-state NMR spectrometer was used at the Korea Basic Science Institute. Magic-angle-spinning (MAS) ^{13}C spectra were obtained at 240.0 K by packing the hydrate samples. All ^{13}C NMR spectra were collected at the Larmor frequency of 100.4 MHz, with MAS at 2.4 kHz. A contact pulse-length of 2 ms and pulse-repetition delay of 10 s under proton decoupling, were employed with radio-frequency field strengths of 50 kHz on both proton and carbon channels. The carbon resonance peak of tetramethylsilane (TMS), assigned to a chemical shift of 0 ppm at 300.0 K, was used as the external chemical-shift reference.

RESULTS AND DISCUSSION

Fig. 1 shows ^{13}C MAS NMR stacked spectra of $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + 5.56\ \text{mol\% THF}$ mixed hydrates formed using various C_2H_4 and C_2H_6 feed-gas compositions. The feed gas compositions were 20% $\text{C}_2\text{H}_4 + 80\% \text{C}_2\text{H}_6$, 40% $\text{C}_2\text{H}_4 + 60\% \text{C}_2\text{H}_6$, 60% $\text{C}_2\text{H}_4 + 40\% \text{C}_2\text{H}_6$, and 80% $\text{C}_2\text{H}_4 + 20\% \text{C}_2\text{H}_6$. The guest molecules enclosed in small and large cavities showed different chemical shifts in the NMR spectra. Due to this difference in chemical shifts, the hydrate structure could be determined from the NMR peaks obtained. From the literature [1], C_2H_6 molecules in large cavities of sI and sII appeared at the 7.7 ppm and 6.5 ppm in NMR spectra using tetramethylsilane (TMS) as a standard. The atomic signal in the up-field region at 7.3 ppm (Fig. 1) is due to C_2H_6 molecules in large cavities of sII, and the faint signal at 6.7 ppm is from gas molecules. Although the difference between C_2H_6 molecules in large sI and sII cavities is about $\Delta = 1.1\ \text{ppm}$, no atomic resonance near 6.2 ppm was observed. Moreover, several papers report that chemical shift of C_2H_6 in large cavities of sI was observed at 7.3 ppm [10,15]. THF molecules were

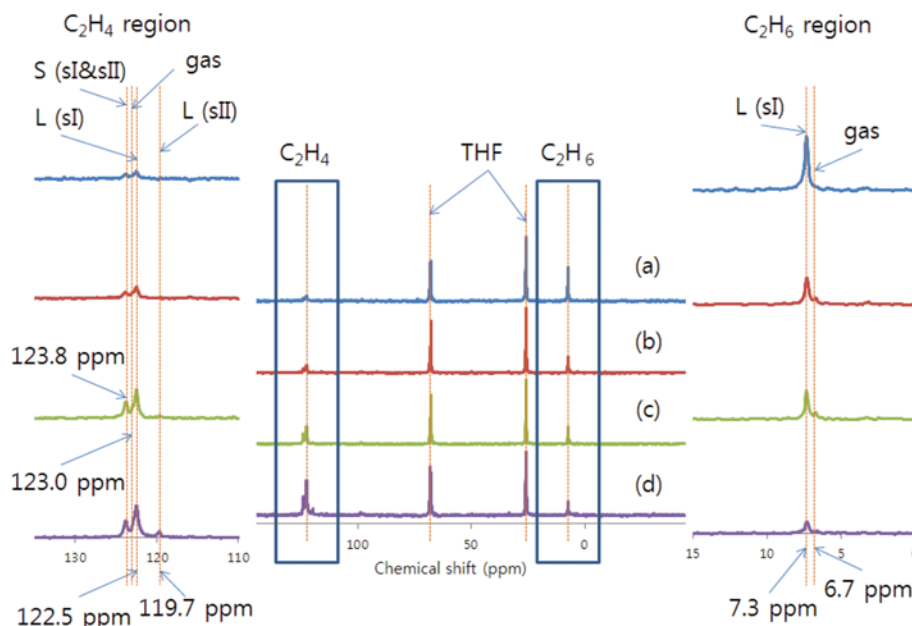


Fig. 1. Solid-state ^{13}C MAS NMR spectra of $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + 5.56\ \text{mol\% THF}$ mixed hydrates formed under the various C_2H_4 and C_2H_6 feed gas composition; feed gas composition (a) 20% $\text{C}_2\text{H}_4 + 80\% \text{C}_2\text{H}_6$ (b) 40% $\text{C}_2\text{H}_4 + 60\% \text{C}_2\text{H}_6$ (c) 60% $\text{C}_2\text{H}_4 + 40\% \text{C}_2\text{H}_6$ (d) 80% $\text{C}_2\text{H}_4 + 20\% \text{C}_2\text{H}_6$.

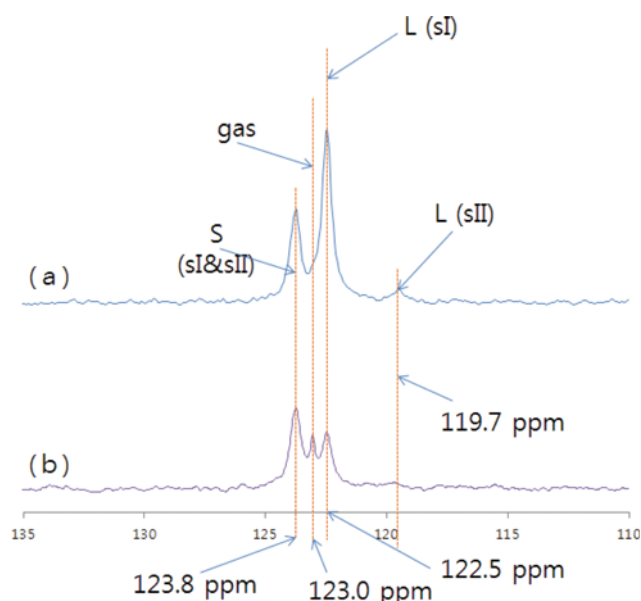


Fig. 2. Solid-state ^{13}C MAS NMR spectra of the C_2H_4 +THF mixed hydrates formed under the pure C_2H_4 gas; (a) 5.56 mol% THF (b) 10.0 mol% THF.

captured in large cavities and identified by two resonances ($-\text{C}-\text{C}-$ at 25.8 ppm and $-\text{C}-\text{O}-\text{C}-$ at 68.0 ppm). However, the atomic resonances in the downfield region (119.7–123.8 ppm in Fig. 1) are due to C_2H_4 molecules. In the magnified NMR spectra in the C_2H_4 region of Fig. 1, convoluted NMR spectra having peaks of 123.8, 123.0, 122.5, and 119.7 ppm, were observed. The C_2H_4 NMR peaks observed were reported in previous research [10]. The atomic signal at 122.5 ppm and the small signal at 123.8 ppm were supposed to be due to C_2H_4 molecule in large cavities and in small cavities. Moreover, based on the observed peak positions for C_2H_4 , it could be concluded that the hydrate crystal structure of the sample was sI. Fig. 2 shows the results of ^{13}C MAS NMR spectra for (a) the 5.56 mol% mixed THF hydrates, and (b) the 10.0 mol% mixed THF hydrates formed with 100% C_2H_4 feed-gas. Theoretically, because pure THF forms sII hydrates with 17 water molecules per THF molecule, the stoichiometry of THF solutions becomes 5.56 mol%, which is the highest host-to-guest ratio for forming a clathrate hydrate. In most cases, THF is mixed with light gas molecules (disregarding heavy hydrocarbons), as a promoter to form hydrates at higher temperature and lower pressure. However, C_2H_4 and C_2H_6 mixed THF hydrates need lower temperature and higher pressure than formation conditions of pure C_2H_4 and C_2H_6 hydrates [13,14]. For example, while 6 mol% THF- C_2H_4 hydrates were formed at about 279 K and 20 bar, the formation temperature of pure C_2H_4 and C_2H_6 hy-

drates at 20 bar was about 285 K. In those cases, it should be noted that THF inhibited formation of the hydrates. Returning to Fig. 2, the resonance peak intensity of C_2H_4 molecules in sI large cavities decreased with increasing THF concentration. This could be attributed to competition of C_2H_4 and C_2H_6 guest molecules with THF molecules to occupy the large cavities. In 10.0 mol% THF- C_2H_4 hydrates, the extra THF molecules were thought to prevent C_2H_4 from occupying the large cavities of sII hydrates. This is other evidence showing that the 122.5 ppm chemical shift is from C_2H_4 molecules in large sI cavities. Whereas, the resonance peak of C_2H_4 molecules in sII cavities was observed at 119.7 ppm only in 5.56 mol% THF- C_2H_4 hydrates. It is thought that C_2H_4 molecules could enter large, unoccupied sII cavities due to THF tuning phenomena and the non-stoichiometric feature of clathrate hydrates. From the literature [16], the chemical shift of C_2H_4 gas phase is known to be 123.5 ppm. The excess THF could make the prepared hydrates dissociate due to the inhibition effect of THF, considering C_2H_4 , during the process of preparing or analyzing the sample of 10.0 mol% THF- C_2H_4 hydrates. The small cavities of sI and sII are the same structure, both having a pentagonal dodecahedron (12-sided cavity). Using the static NMR technique, Seo et al. [17] reported that small cavities of sI hydrate have pseudo-spherical symmetry, but small cavities of sII hydrate have an asymmetric shape. However, no difference could be observed between the small cavities of sI and sII structures using the MAS NMR technique. According to above evidence, it was concluded that the atomic signal at 123.8 ppm is due to C_2H_4 molecules in small cavities of both sI and sII.

The respective NMR peak areas obtained using ^{13}C MAS NMR stacked spectra of C_2H_4 + C_2H_6 +5.56 mol% THF mixed hydrates formed under various C_2H_4 and C_2H_6 feed-gas compositions were evaluated in arbitrary units (a.u.). The calculated and identified results are shown in Fig. 1. Peak deconvolution of these results due to the low-resolution power of a 400 MHz NMR spectrometer was performed by using OriginPro 9.0 software (OriginLab, USA). Representative NMR sample results for the feed-gas composition of 80% C_2H_4 +20% C_2H_6 are shown in Fig. 3. Fitting was done using Lorentz multi-peak fit and the THF peak area was ignored. From these estimated results, the mole fraction of C_2H_4 and C_2H_6 entrapped in hydrate lattice depending on the feeding gas was determined and summarized in Table 2. Note that, as shown in the table, the mole fraction of C_2H_4 in the hydrate matrix was higher than the mole fraction of C_2H_4 in feed gas. The NMR analysis indicates that the reason would be that C_2H_4 molecules could be contained in both small and large cavities, while C_2H_6 molecules could be encaged only in large cavities of sII. In other words, it could be that the phenomenon occurs due to differences in the molecular size of C_2H_4 and C_2H_6 . From the literature [1], the diam-

Table 1. The NMR peak area (arbitrary unit) of C_2H_4 + C_2H_6 +5.56 mol% THF mixed hydrates formed under the various feed gas compositions

Feed gas	C_2H_4 peak area (a.u.) of S cage sI&sII	C_2H_4 peak area (a.u.) of L cage sI	C_2H_4 peak area (a.u.) of L cage sII	C_2H_6 peak area (a.u.) of L cage sI
20% C_2H_4 +80% C_2H_6	8.97	14.18	0.00	50.40
40% C_2H_4 +60% C_2H_6	34.35	21.73	0.00	42.22
60% C_2H_4 +40% C_2H_6	61.30	103.03	0.00	52.26
80% C_2H_4 +20% C_2H_6	104.09	39.11	12.72	19.48

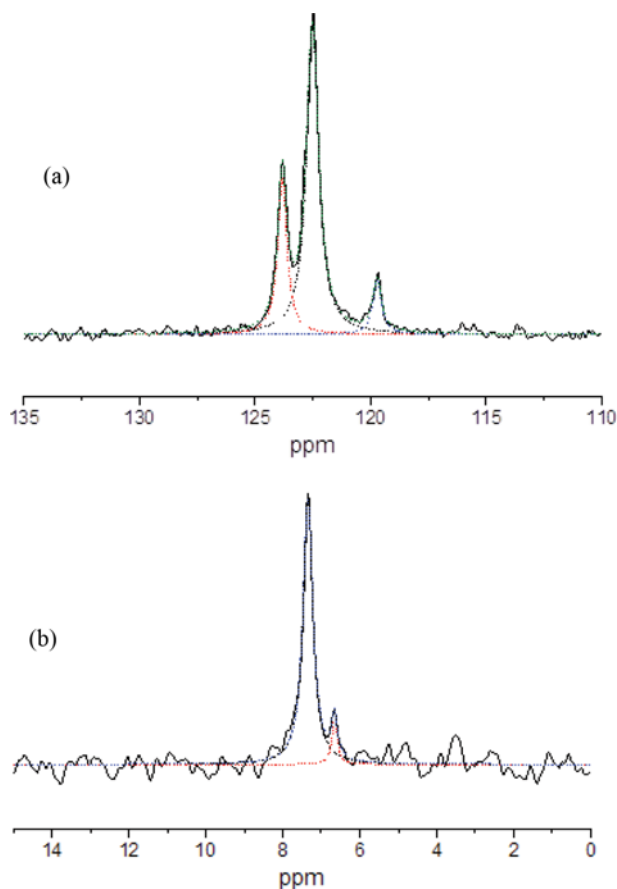


Fig. 3. Peak deconvolution of solid-state ^{13}C MAS NMR spectra of $\text{C}_2\text{H}_4+\text{C}_2\text{H}_6+5.56\text{ mol\% THF}$ mixed hydrates formed under the 80% C_2H_4 and 20% C_2H_6 feed gas composition; (a) downfield region showing atomic signals of C_2H_4 molecules, and (b) upfield region showing atomic signals of C_2H_6 molecules.

Table 2. C_2H_4 and C_2H_6 mole fraction in the hydrate lattice of $\text{C}_2\text{H}_4+\text{C}_2\text{H}_6+5.56\text{ mol\% THF}$ mixed hydrates formed under the various feed gas compositions

Feed gas	C_2H_4 fraction	C_2H_6 fraction
20% C_2H_4 +80% C_2H_6	0.31	0.69
40% C_2H_4 +60% C_2H_6	0.57	0.43
60% C_2H_4 +40% C_2H_6	0.76	0.24
80% C_2H_4 +20% C_2H_6	0.89	0.11

eters of the small cavities in sI and sII are about 5.1 Å and 5.0 Å, and the molecular sizes of C_2H_4 and C_2H_6 are 5.2 Å and 5.5 Å, respectively. The respective ratios of molecular diameter (of C_2H_4 and C_2H_6) to cavity diameter (small cavities in sI) are 1.02 and 1.08. Therefore, while C_2H_4 molecules could change their conformation to fill the small cavities, C_2H_6 molecules are too large to fit into them. It is concluded that these molecular size differences could provide the selectivity characteristics desired for gas enclathration.

The NMR spectroscopic analysis could provide the fundamental information needed for developing a C_2H_4 and C_2H_6 process for separation by repeated hydrate formation and dissociation. Fig. 4 is a conceptual diagram for C_2H_4 and C_2H_6 separation process,

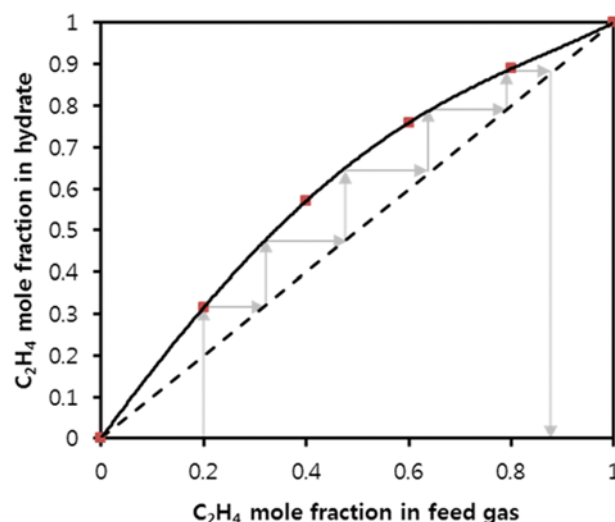


Fig. 4. C_2H_4 and C_2H_6 mole fraction in hydrate lattice of $\text{C}_2\text{H}_4+\text{C}_2\text{H}_6+5.56\text{ mol\% THF}$ mixed hydrates formed under the various C_2H_4 and C_2H_6 feed gas composition.

which was drawn from the data of feed gas composition and gas composition in the hydrate lattice obtained by NMR quantitative analysis. Microsoft® Excel 2010 was used to calculate the regression equation. The coefficients of the equation were determined by fifth-order polynomial curve fitting with R-squared value=1.00 (see Supplementary Information), shown as solid line in Fig. 4. The number of theoretical hydrate formation and dissociation cycles for C_2H_4 purification was estimated by using the regression equation in the cases of feed gases containing 20.0% and 80.0% C_2H_4 , respectively (Tables S1 and S2). When C_2H_4 and C_2H_6 mixed gas containing 20.0% C_2H_4 was fed into a separation process using gas hydrate, the resulting concentration of C_2H_4 in the hydrate was 31.4% on the first cycle. The gas mixture released from this hydrate could be used to form hydrate again on the second cycle, and after five cycles of formation and dissociation, a recovery of more than 88% of the C_2H_4 in the gas mixture could be achieved, as illustrated in Fig. 4. Theoretically, after 15 cycles of formation and dissociation, polymer grade C_2H_4 (>99.9%) could be obtained (Table S2). The ethylene yield is over 80% after ethane cracking. In the case of a feed-gas mixture with 80% C_2H_4 and 20% C_2H_6 , 11 cycles of hydrate separation would be needed to produce polymer grade C_2H_4 . Although additional modifications may be required for industrial application, the experimental results obtained in this study suggest that the hydrate-based process could be used for C_2H_4 and C_2H_6 separation.

CONCLUSIONS

$\text{C}_2\text{H}_4+\text{C}_2\text{H}_6+5.56\text{ mol\% THF}$ mixed hydrates formed with various feed gas compositions of 100% C_2H_4 , 20% C_2H_4 +80% C_2H_6 , 40% C_2H_4 +60% C_2H_6 , 60% C_2H_4 +40% C_2H_6 , and 80% C_2H_4 +20% C_2H_6 were analyzed using the ^{13}C MAS NMR spectroscopic method. In addition, $\text{C}_2\text{H}_4+5.56\text{ mol\% THF}$ and $\text{C}_2\text{H}_4+10.0\text{ mol\% THF}$ mixed hydrates samples were prepared for identification of C_2H_4 peaks observed in the downfield area of ^{13}C NMR. The atomic signal at 122.5 ppm and a small signal at 123.8 ppm were due to C_2H_4

molecule in large and small cavities, respectively. The atomic signal in the up-field region at 7.3 ppm was due to C_2H_6 molecules in large cavities of sII. Thus, C_2H_4 molecules can occupy both small and large cavities of sI and sII, while C_2H_6 molecules can occupy only the large cavities of sI.

The respective NMR peak areas obtained using ^{13}C MAS NMR stacked spectra of $C_2H_4+C_2H_6+5.56$ mol% THF mixed hydrates formed under various C_2H_4 and C_2H_6 feed gas compositions, were evaluated and calculated after peak deconvolution using Lorentz multi-peak fit. The quantitative analysis results of the NMR spectra provided a ratio of C_2H_4 and C_2H_6 in the hydrate lattice. The mole fraction of C_2H_4 in the hydrate matrix was found to increase with increasing feed ratio of C_2H_4 . Based on NMR analysis, a hydrate-based process for separating C_2H_4 and C_2H_6 by repeated hydrate formation and dissociation was proposed. In the case of the feed-gas mixture with 20% C_2H_4 and 80% C_2H_6 , a recovery of more than 88% C_2H_4 in the gas mixture could be achieved after five cycles of the hydrate-based separation process. The qualitative and quantitative results obtained in this investigation provide fundamental data useful for designing and evaluating a clathrate-based process for separating C_2H_4 and C_2H_6 .

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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Supporting Information

¹³C NMR analysis of C₂H₆+C₂H₄+THF mixed hydrate for an application to separation of C₂H₄ and C₂H₆

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Table S1. The number of theoretical hydrate formation and dissociation cycles for C₂H₄ purification in the cases of feed gases containing 80.0% C₂H₄

Feed gas composition	Hydrate composition	Cycles
0.8	0.888959	1
0.888960	0.937056	2
0.937057	0.963233	3
0.963234	0.978045	4
0.978045	0.986701	5
0.986701	0.991870	6
0.991873	0.995005	7
0.995005	0.996920	8
0.996920	0.998096	9
0.998097	0.998822	10
0.998822	0.999270	11

<Polynomial Equation>

$$y=0.2992x^5-0.1334x^4-0.3138x^3-0.5489x^2+1.6969x$$

$$R^2=1.0000$$

Table S2. The number of theoretical hydrate formation and dissociation cycles for C₂H₄ purification in the cases of feed gases containing 20.0% C₂H₄

Feed gas composition	Hydrate composition	Cycles
0.2	0.314796	1
0.314796	0.469609	2
0.469609	0.643676	3
0.643676	0.791308	4
0.791308	0.884107	5
0.884107	0.934456	6
0.934456	0.961790	7
0.961790	0.977213	8
0.977213	0.986209	9
0.986209	0.991576	10
0.991576	0.994825	11
0.994825	0.996809	12
0.996809	0.998029	13
0.998029	0.998780	14
0.998780	0.999245	15