Chemical Engineering Journal 161 (2010) 308–312

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Short communication

Enhancing CO_2 separation for pre-combustion capture with hydrate formation in silica gel pore structure

Yutaek Seo[a], Seong-Pil Kang[b,*]

[a] CSIRO Petroleum Resources, 26 Dick Perry Avenue, Kensington, Perth, WA 6151, Australia
[b] Clean Fossil Energy Research Center, Korea Institute of Energy Research, 71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, Republic of Korea

ARTICLE INFO

Article history:
Received 2 March 2010
Received in revised form 15 April 2010
Accepted 16 April 2010

Keywords:
Gas hydrate
CO_2
Separation
Silica gel
Pre-combustion
Capture

ABSTRACT

This communication reports the enrichment of the hydrate phase with CO_2 in gas hydrates formed from a CO_2 and H_2 gas mixture when using silica gels to form the hydrate. Phase composition analysis showed that the CO_2 concentrations in the retrieved gas from hydrates were in the range of 96.5 and 98.7 mol% at the range of 6.0–9.2 MPa at 274.15 K in 100 nm silica gel. ^{13}C NMR spectra supplemented the phase composition analysis and suggested that CO_2 molecules occupy 93% of small cages and 100% of large cages in the hydrate phase. It is noted that the obtained CO_2-rich hydrate, by implementing a silica gel pore structure, has a composition of $(0.14H_2/1.86\ CO_2)_S\cdot(6CO_2)_L\cdot 46H_2O$, which provides the quite promising idea of separating CO_2 from an industrial gas containing H_2 such as shifted synthesis gas, for pre-combustion capture.

1. Introduction

The growing recognition on current global warming and climate change has raised a number of issues, especially how to reduce anthropogenic CO_2 emissions and to stabilize the atmospheric CO_2 concentration. As such, various possible scenarios including injecting CO_2 into geologic formations for enhanced oil recovery, the use of CO_2 as an industrial consumable, and chemically transforming CO_2 into minerals have been discussed as possible methods to tackle those challenges [1]. At the same time, the absorption or adsorption of CO_2 from industrial gas streams has been proposed to separate and concentrate CO_2 before transportation to sequestration site [2]. There have been two approaches to CO_2 capture either as CO_2 is separated from the combustion flue gas (post-combustion capture) or as it is separated before the shifted synthesis gas is combusted (pre-combustion capture).

Gas hydrates, known as non-stoichiometric crystalline compounds [3], represent an attractive method for the above two approaches because when a gas mixture including CO_2 forms gas hydrate, the concentration of CO_2 in the hydrate phase becomes much higher than that of the vapor phase due to the fractionation effect [4–6]. Therefore the equilibrium conditions of mixed hydrates and the distribution of CO_2 in hydrate cages have been of primary interest in the development of potential separation processes. To date there have been extensive efforts to understand the thermodynamic properties of mixed hydrate formed from either CO_2 and N_2 or CO_2 and H_2 gas mixture, which are the main components of combustion flue gas or shifted synthesis gas, respectively [7–9].

Although the thermodynamic studies and structural analyses present the possibilities of developing separation technology, a weak point of these results is that several stages are required to obtain a high concentration of CO_2 stream from feed gas, which reduces the economics of the separation process. Previous results suggest that at least two stages of the separation process will be required to obtain a concentrated CO_2 gas stream from the post-combustion gas stream, and, further, have demonstrated that an additional stage might be required if the promotion of hydrate formation is implemented by adding THF [4]. It was also suggested that the hybrid separation process could be one of several possible options for separating CO_2 from shifted synthesis gas, in which a membrane reactor is used to purify the H_2-rich streams [9]. In our previous work, in attempting to understand the structural characteristics of gas hydrate formed in silica gel pore structures, we determined that hydrate formation in confined structures such as silica gel pore structures shows a higher formation rate and enhanced fractionation effect than in the bulk water phase [4,10]. This unique enclathration characteristic provides insight into the possibility of implementing silica gels in the hydrate-based CO_2 separation process, especially in pre-combustion capture. We carried out the composition analysis of the hydrate phase to quantify the CO_2 fractionation over hydrate cages and used solid-state NMR

---

* Corresponding author. Tel.: +82 42 860 3475; fax: +82 42 860 3034.
E-mail address: spkang@kier.re.kr (S.-P. Kang).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.04.032

spectroscopy to investigate the spectral pattern of mixed hydrate in bulk water and silica gel. These results have led to the concept of enhancing fractionation of CO_2 in the hydrate phase, which shows the possibility of obtaining CO_2-rich hydrate product for pre-combustion capture.

2. Experiments

The gas mixture used in this study was supplied by World Gas and had a UHP grade and HPLC grade water was supplied by Sigma–Aldrich Chemicals Co. with a purity of 99.99 mol%. Spherical silica gel particles with nominal pore diameter of 30 and100 nm were purchased from Silicycle.

The apparatus for gas composition analysis consists of a 316 SUS cylindrical reactor with a temperature control system. The reactor had an internal volume of about 500 cm^3. The reactor was equipped with a motor-driven impeller to enhance the conversion of water to hydrate, while stirring is not used for the silica gel particles. The temperature of the reactor was controlled by an externally circulating refrigerator/heater, and a K-type thermocouple probe with a digital thermometer was inserted into the reactor to measure the actual temperature of its contents. The pressure of the system was measured by a digital pressure gauge of which the span and resolution was 0–10.0 MPa and 0.25% of full scale. The composition of the vapor phase and retrieved gas from hydrate phase were measured by gas chromatograph. The water preloaded silica gels are prepared by water sorption by placing dried silica gels in a bottle with 85 wt% of water to the pore volume of silica gel. After mixing, the bottle was sealed off to prevent water evaporation and was vibrated with an ultrasonic wave at room temperature for at least 12 h to obtain complete filling of water in the pores. The experiment for hydrate formation was commenced by charging the reactor with about 150 cm^3 of silica gel containing pore water. After the reactor was cooled down to 274.15 K and the temperature was stabilized, a vacuum pump was used to remove the remaining air inside. Then the gas mixture of carbon dioxide and hydrogen was charged to the reactor to desired pressure. As the gas in the reactor was consumed due to hydrate formation, the temperature and pressure in the reactor had been monitored for at least 24 h to ensure the complete of hydrate formation. When the pressure was in steady state for more than 12 h, the final composition of the vapor phases were measured by gas chromatograph. After the completion of hydrate formation, vapor phase was discharged quickly and evacuation was effected to initiate the dissociation of the hydrate phase. The temperature increased to around 300 K to enhance the dissociation process. When the temperature and pressure were in steady state, the composition of the retrieved gas from the hydrate phase was measured as the composition of hydrate phase. The detailed apparatus and procedures can be found in our previous work [11]. Test runs for the adsorption of carbon dioxide to dried silica gel particles were also performed using the same procedure. The adsorbed amount of carbon dioxide to silica gel that we measured was so small and was negligible.

For studies of structural characteristics, mixed H_2 and CO_2 hydrates were prepared in porous silica gel (silicycle, pore size 30 and 100 nm). ^{13}C cross-polarization (CP) NMR spectra were recorded at 240 K by placing the hydrate sample in a 4 mm o.d. Zr-rotor that was loaded into the variable temperature (VT) probe on a Bruker 400 MHz solid-state NMR spectrometer. All spectra were recorded at a Larmor frequency of 100.6 MHz with the cross-polarization time of 2 ms. High-power proton decoupling (HPDEC) was applied to the sample during data acquisition. The pulse length for proton was 4.2 μs and a pulse repetition delay of 2 s was employed. The downfield carbon resonance peak of adamantane, assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference. $^{13}CO_2$ gas was used to obtain higher intensity CO_2 peaks for pure and mixed hydrates.

Table 1
Composition of vapor and hydrate phase in bulk water and silica gel (100 nm) at 274.15 K and corresponding pressure.

Pressure (MPa)	Composition (mol%CO_2)	
	Vapor	Hydrate
Bulk water		
8.9	26.0	83.2
7.8	27.1	83.8
6.5	28.5	84.5
Silica gel		
9.2	26.7	98.7
8.1	27.8	98.3
7.0	29.1	98.1
6.4	31.0	97.5
6.0	32.5	96.5

3. Results and discussion

Phase equilibrium studies of mixed H_2 and CO_2 hydrate have been carried out to identify phase equilibrium conditions and composition of each phase in equilibrium [6,8,9]. However, the physical properties of the mixed hydrate formed inside the silica gel pore structure have not been investigated thoroughly; therefore, these have to be analyzed before judging the possibility of developing hydrate-based CO_2 separation process from synthesis gas.

First, we used gas uptake measurement and composition analysis of retrieved gas from mixed hydrate. The mixed H_2 and CO_2 hydrates are formed from 41 mol% CO_2 and balanced H_2 gas mixture in considering the composition of treated synthesis gas from a gasifier. After completing the formation of the mixed hydrates in bulk water and silica gels, the pressure and the composition of vapor phase have been recorded, and then vapor phase is discharged quickly to induce the dissociation of mixed hydrates. The retrieved gas is sampled and analyzed with a gas chromatograph. The final pressure and composition of each phase have been represented in Table 1. It shows that the mixed hydrate gives 84.5 mol% CO_2 and balanced H_2 when it is formed from bulk water with 41.0 mol% of CO_2 and balanced H_2 gas mixture at 274.15 K and 6.5 MPa. The composition of the retrieved gas from mixed hydrate formed in bulk water shows a range of 83.2 and 84.5 mol% CO_2 at a pressure range of 6.5 and 8.9 MPa, which is in good agreement with the values in the literature [9]. It should be noted that the decrease of CO_2 concentration in the hydrate phase has been observed when increasing the pressure, as seen in Table 1. A similar trend is reported in the literature [9] and suggests the increase of H_2 occupancy in hydrate cages due to the increase of the pressure.

Subsequently we formed mixed hydrate by contacting water inside silica gel pores of 100 nm diameter with 41.5 mol% CO_2 and balanced H_2 gas mixture at 274.15 K; the pressure has been increased from 6.0 to 9.2 MPa, as shown in Table 1 and Fig. 1. When the mixed hydrate is formed at 274.15 K and 6.0 MPa, the resulting composition of the hydrate phase is 96.5 mol% CO_2 and balanced H_2, which values are higher than those for the mixed hydrate from bulk water at 274.15 K and 6.5 MPa. By increasing the pressure to 9.2 MPa, the CO_2 composition in the hydrate phase increases to 98.7 mol%, which indicates that considerable enrichment of CO_2 in the hydrate phase takes place at corresponding hydrate formation conditions. In particular, the concentration of CO_2 in the hydrate phase formed in silica gels increases with increasing formation pressure, which is a result opposite to results for formation in bulk water. It is obvious that the occupancy of guest molecules in gas hydrate is affected by the silica gel pore structures; accordingly, further studies of structural characteristics of

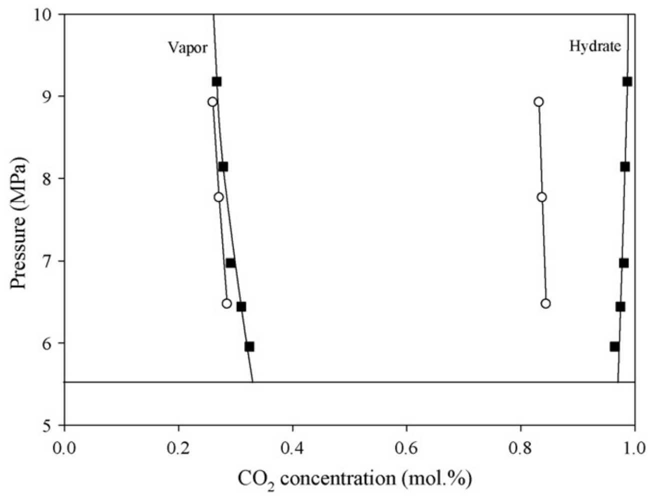

Fig. 1. Composition analysis of vapor and hydrate phase in 100 nm silica gel at formation temperature of 274.15 K. Feed gas composition is 41 mol% CO_2 and balanced H_2. Circles indicate the results from bulk water and squares from silica gel.

the mixed hydrates in silica gel have been carried out with NMR spectroscopy.

For H_2 and CO_2 gas mixtures containing more than 20 mol% of CO_2, the mixed H_2 and CO_2 hydrate is known to form structure I, as does pure CO_2, composed of two pentagonal dodecahedra (5^{12}) and six tetrakaidecahedra ($5^{12}6^2$) cages. The X-ray diffraction pattern of the mixed hydrate identifies the crystal structure with a cubic unit cell parameter of 1.186 nm; the ^{13}C NMR spectra of mixed hydrate suggests that the CO_2 molecules occupy a large amount of 5^{12} and $5^{12}6^2$ cages, while H_2 resides in 5^{12} cages [12]. Quantitative estimates of cage occupancy are provided based on the analysis of the IR spectra and the knowledge of hydrate gas composition from the gas chromatograph [13,14]. Although ^{13}C NMR spectroscopy provides only the superimposed spectral pattern of CO_2 in small and large cages, it still provides important information on the molecular dynamics of CO_2 in hydrate cages, which can be distinguished with a chemical shift anisotropy induced by the cage symmetry [15]. Combining the ^{13}C NMR spectra analysis and hydrate composition measurement will provide molecular distribution in specific hydrate structures. Moreover, the structural characteristics of the mixed hydrate have not been considered yet when the mixed hydrate is confined in the silica gel pore structure.

For CO_2 trapped in hydrate cages, chemical shift anisotropy has been induced by asymmetry in the immediate environment of the molecules as shown in the ^{13}C cross-polarization (CP) NMR spectrum of H_2 and the CO_2 hydrate from bulk water, shown in Fig. 2(a). For mixed hydrate in bulk water, a sharp peak for CO_2 in 5^{12} cages is present at δ_{iso} of 126.2 ppm. For mixed hydrates in silica gels, δ_{iso} for CO_2 in 5^{12} cages appears at 137.3 ppm (100 nm) and 137.8 ppm (30 nm). The chemical shift anisotropies for CO_2 in $5^{12}6^2$ cages are −53.7 ppm for 100 nm and −52.2 ppm for 30 nm, as shown in Fig. 2(b) and (c), respectively. We note that the broad peak for CO_2 in 5^{12} cages appears more distinctive for mixed hydrates in silica gels than it does in bulk water, which might suggest that the amount of CO_2 molecules in 5^{12} cages is increased during the formation of the mixed hydrate inside the silica gel pore structures.

When considering the data from ^{13}C NMR spectra and composition analysis, along with the assumption of H_2 molecules residing in small cages, cage occupancy of mixed hydrate can be estimated, and it can be demonstrated that CO_2 occupies 93% of small cages and 100% of large cages of mixed hydrate that is confined in silica gel pores. This premise gives a CO_2-rich hydrate product having the composition of $(0.14H_2/1.86CO_2)_S{\cdot}(6CO_2)_L{\cdot}46H_2O$ at 274.15 K and 8.1 MPa. In this work, the occupancy of H_2 in small cages, θ_{S,H_2}, is decreased from 0.23 for mixed hydrate in bulk water [14] to 0.07 for mixed hydrate in silica gels. This suggests that the pore structure of silica gel plays an important role, in which the transport of CO_2 and H_2 molecules during the formation of mixed hydrate is affected by the Langmuir isotherm of each molecule. It is likely that the initial formation of mixed hydrate inside silica gel pores involves both CO_2 and H_2 molecules; however, in progress of mixed hydrate formation, CO_2 molecules are dominantly transported inside the pore structure and H_2 molecules reside in vapor phase or the inlet of pores, resulting in enrichment of the hydrate phase with CO_2.

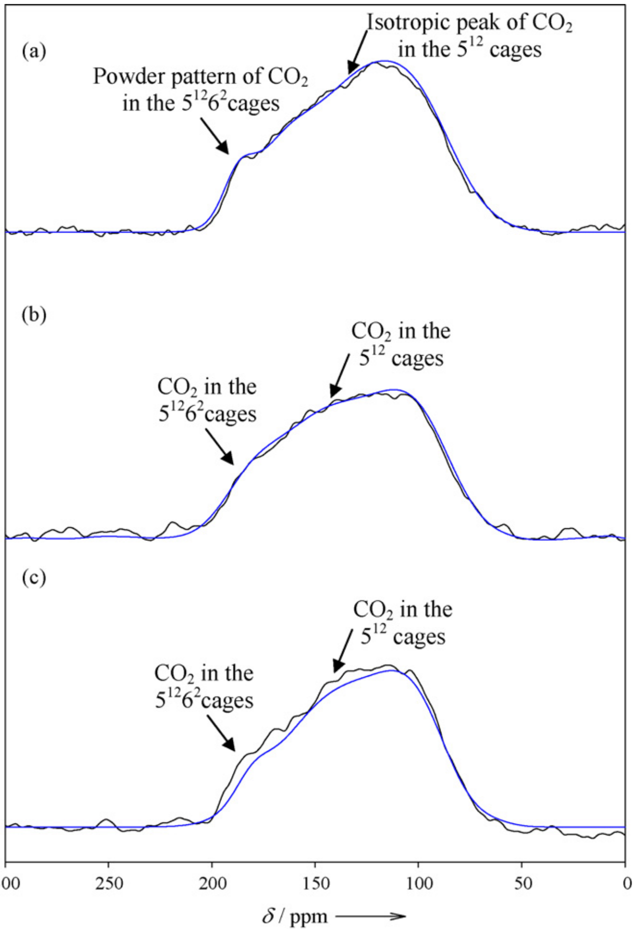

Fig. 2. ^{13}C NMR spectra of mixed H_2 + CO_2 hydrate in (a) bulk water, (b) 100 nm silica gel, and (c) 30 nm silica gel. Blue lines indicate resolved peaks using NMR peaks analysis software. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Additional experiments are still required to give a complete explanation of the enhancement of CO_2 fractionation in the hydrate phase when it forms in silica gel pore structures. The effect of the experimental conditions such as temperature and pore size of silica gel will provide important information to optimize formation rate and conversion ratio of water to hydrate. However, on the basis of current experimental results, it is clear that the formation of hydrate in silica gel pore structures offers the great possibility of separating CO_2 from shifted synthesis gas. Although the details of the process still need to be optimized, it is possible to consider the conceptual design of the separation process. One of the possible types proposed for the reactor might be a series of fixed-bed reactors for successive formation and dissociation processes, as shown in Fig. 3(a). The synthesis gas is injected into the first reactor while not being injected into the second reactor by closing valve 2, and then the synthesis gas contacts with water in the silica gel pore

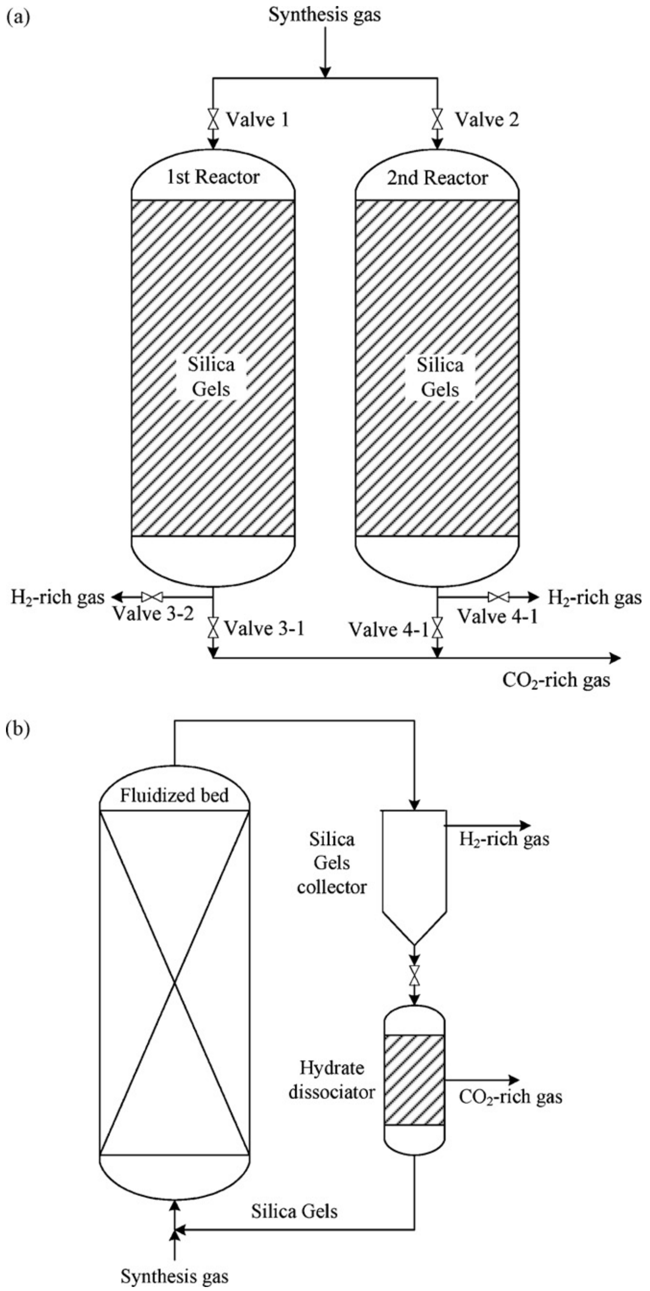

Fig. 3. Schematic diagram of hydrate-based CO_2 separation process using silica gel for hydrate formation. (a) Series reactors type, (b) fluidized bed type.

to form hydrate. Once the pressure of the first reactor reaches a desired value, valve 1 is closed and the hydrate formation takes place with a designated rate at corresponding conditions. After completion of hydrate formation, the reactor is conditioned for hydrate dissociation by flushing the gas phase, which would go to next treatment step, for example a membrane separator [9]. During the hydrate formation in the first reactor, valve 2 opens just after closing valve 1, and the synthesis gas is directed to the second reactor, in which the temperature is already set for the next hydrate formation. The required number and volume of reactors would be determined by the total volume of shifted synthesis gas to be treated in a given time; however, the continuous separation of CO_2 from shifted synthesis gas can be achieved with the sequential operation of a series of reactors. Any means of enhancing this kind of reactor is open to consideration. Another type of reactor would be a fluidized bed reactor, because silica gel particles containing water in pore structures are known to be suitable for fluidization. Injected synthesis gas and silica gel particles would make contact at the bottom of the reactor, and then move up by gas flow to where CO_2 in synthesis gas enclathrated into hydrate cages would form in silica gel pore structures. The particles containing CO_2-rich hydrate can be collected and separated for the next step, which seems similar to the circulated fluidized bed reactor. Of course, to meet the yield for separation, the fluidized bed must provide enough contact time between the synthesis gas and the silica gel particles.

More studies on operation conditions are needed to improve the economy of the process; however, it is obvious that silica gels containing water in pore structures provide more flexible design options for a hydrate-based per-combustion CO_2 capture process.

4. Conclusions

The results presented here show that, at least in a laboratory setting, the enrichment of the hydrate phase with CO_2 is favoured by using silica gels both from the points of view of ^{13}C NMR analysis and phase composition analysis. Hydrate formation from 41 mol% CO_2 and balanced H_2 gas mixture showed that most of the cages are occupied by CO_2 molecules, and that a 98.7 mol% CO_2 and balanced H_2 gas mixture is retrieved from the dissociation of hydrate formed at ~9.2 MPa and 274.15 K. When decreasing the pressure from 9.2 MPa to 6.0 MPa, the concentration of CO_2 in the hydrate phase decreases from 98.7 to 96.5 mol%, which is a tendency opposite to that in bulk water. ^{13}C NMR spectra suggest that major changes of CO_2 distribution happen in small cages, which may indicate the effect of pore structure on the formation of mixed hydrate. Current industrial concepts such as a series of fixed-bed reactors and a fluidized bed reactor are discussed as possible design options for a hydrate-based pre-combustion CO_2 capture process.

Acknowledgements

This research was funded by the KETEP (Korea Institute of Energy and Resources Technology Evaluation and Planning). The authors thank Dr. Chang Hyun Ko (KIER) for helpful comments and discussions regarding this work.

References

[1] S.H. Stevens, V.A. Kuuskraa, J. Gale, D. Beecy, CO_2 injection and sequestration in depleted oil and gas fields and deep coal seams: worldwide potential and costs, Environ. Geosci. 8 (2001) 200–209.
[2] W. Arlt, Engineering solutions for limiting the increase of atmospheric carbon dioxide, Chem. Eng. Technol. 26 (2003) 1217–1224.
[3] E.D. Sloan, Clathrate Hydrates of Natural Gases, third edition, CRC Press, Boca Raton, 2008.
[4] (a) S.P. Kang, H. Lee, Recovery of CO_2 from flue gas using gas hydrate: thermodynamic verification through phase equilibrium measurements, Environ. Sci. Technol. 34 (2000) 4397–4400;
(b) Y. Seo, I.L. Moudrakovski, J.A. Ripmeester, J.-W. Lee, H. Lee, Efficient recovery of CO_2 from flue gas by clathrate hydrate formation in porous silica gels, Environ. Sci. Technol. 39 (2005) 2315–2319.
[5] D. Yang, L.A. Le, R.J.M. Martinez, R.P. Currer, D.F. Spencer, G. Deppe, Heat transfer during CO_2 hydrate formation in a continuous flow reactor, Energy Fuels 22 (2008) 2649–2659.
[6] R. Kumar, H. Wu, P. Englezos, Incipient hydrate phase equilibrium for gas mixtures containing hydrogen, carbon dioxide and propane, Fluid Phase Equilib. 244 (2006) 167–171.
[7] P Linga, R. Kumar, P. Englezos, Gas hydrate formation from hydrogen/carbon dioxide and nitrogen/carbon dioxide gas mixtures, Chem. Eng. Sci. 62 (2007) 4268–4276.
[8] P. Linga, A. Adeyemo, P. Englezos, Medium-pressure clathrate hydrate/membrane hybrid process for postcombustion capture of carbon dioxide, Environ. Sci. Technol. 42 (2007) 315–320.
[9] P. Linga, F. Kumar, P. Englezos, The clathrate hydrate process for post and pre-combustion capture of carbon dioxide, J. Hazard. Mater. 149 (2007) 625–629.
[10] Y. Seo, S.-P. Kang, W. Jang, Structure and composition analysis of natural gas hydrates: ^{13}C NMR spectroscopic and gas uptake measurements of mixed gas hydrates, J. Phys. Chem. A 113 (2009) 9641–9649.

[11] S.-P. Kang, Y. Seo, W. Jang, Kinetics of methane and carbon dioxide hydrate formation in silica gel pores, Energy Fuels 23 (2009) 3711–3715.

[12] D.-Y. Kim, H. Lee, Spectroscopic identification of the mixed hydrogen and carbon dioxide clathrate hydrate, J. Am. Chem. Soc. 127 (2005) 9996–9997.

[13] R. Kumar, P. Englezos, I.L. Moudrakovski, J.A. Ripmeester, Structure and composition of CO_2/H_2 and $CO_2/H_2/C_3H_8$ hydrate in relation to simultaneous CO_2 capture and H_2 production, AIChE 55 (2009) 1584–1594.

[14] R. Kumar, S. Lang, P. Englezos, J.A. Ripmeester, Application of the ATR-IR spectroscopic technique to the characterization of hydrates formed by CO_2, CO_2/H_2 and $CO_2/H_2/C_3H_8$, J. Phys. Chem. A 113 (2009) 6308–6313.

[15] J.A. Ripmeester, C.I. Ratcliffe, The diverse nature of dodecahedral cages in clathrate hydrates as revealed by ^{129}Xe and ^{13}C NMR spectroscopy: CO_2 as a small-cage guest, Energy Fuels 12 (1998) 197–200.