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Catalysis Today 115 (2006) 279–282

CATALYSIS TODAY

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Spectroscopic analysis of carbon dioxide and nitrogen mixed gas hydrates in silica gel for CO_2 separation

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Abstract

In this study solid-state NMR spectroscopy was used to identify structure and guest distribution of the mixed $N_2 + CO_2$ hydrates. These results show that it is possible to recover CO_2 from flue gas by forming a mixed hydrate that removes CO_2 preferentially from CO_2/N_2 gas mixture. Hydrate phase equilibria for the ternary CO_2–N_2–water system in silica gel pores were measured, which show that the three-phase H–L_w–V equilibrium curves were shifted to higher pressures at a specific temperature when the concentration of CO_2 in the vapor phase decreased. ^{13}C cross-polarization (CP) NMR spectra of the mixed hydrates at gas compositions of more than 10 mol% CO_2 with the balance N_2 identified that the crystal structure of mixed hydrates as structure I, and that the CO_2 molecules occupy mainly the abundant $5^{12}6^2$ cages. This makes it possible to achieve concentrations of more than 96 mol% CO_2 gas in the product after three cycles of hydrate formation and dissociation.

Keywords: Clathrate hydrate; Nitrogen; Carbon dioxide; Silica gel; ^{13}C NMR analysis

1. Introduction

Gas hydrates should be considered of particular interest to the energy and environmental field because each volume of hydrate can contain as much as 170 volumes of gas at standard temperature and pressure conditions [1]. Formation of CO_2 hydrate in the deep ocean was considered as one of the possible strategies for carbon sequestration [2,3]. Accordingly, it is desirable to recover CO_2 from flue gas by formation of gas hydrate under specific conditions. Gas hydrates are non-stoichiometric crystalline compounds formed when guest molecules of suitable size and shape are incorporated in the well-defined host cages made up of hydrogen bonded water molecules [4]. These compounds exist in three distinct structural families termed, structures I, II, and H. Numerous investigations covering macroscopic phase equilibria and microscopic structure identification of pure and mixed hydrates can been found in various sources [5–8]. Among the common hydrate formers, CO_2 is known to form structure I which has eight cagelike guest sites with 46 water molecules in the unit cell, including two pentagonal dodecahedra (5^{12}) and six tetrakaidecahedra ($5^{12}6^2$), while N_2 forms structure II hydrates which consist of 16 pentagonal dodecahedra, eight hexakaidecahedron ($5^{12}6^4$), and 136 water molecules [1]. Since CO_2 and N_2 are known as major components of flue gas from power plants, it is necessary to understand the structural characteristics of mixed hydrates formed from gas mixtures of CO_2 and N_2 for developing recovery processes for CO_2 by hydrate formation. In spite of its industrial importance, only a few studies have focused on the mixed hydrate of CO_2 and N_2. Kang and Lee [9] chose THF solutions to capture CO_2 by forming a mixed hydrate and measured hydrate equilibrium conditions that include the stabilizing effects of THF guest molecules in the lattice. In the present study, we used pure water adsorbed in silica gel pores to form the hydrate. When a bulk water phase is used, hydrate formation is limited by gas-water contact at the interface. However, CO_2 and N_2 molecules can easily penetrate a bed of silica gel particles saturated with water, and the dispersed water presents a huge surface for contacting gas molecules and forming gas hydrate in silica gel pores. To develop the recovery process of CO_2 from flue gas, dissociation pressures of CO_2 and N_2 hydrates confined in silica gel pores of nominal diameters of 30.0 nm were measured at several CO_2 vapor compositions and the amount of CO_2 occupying hydrate

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doi:10.1016/j.cattod.2006.02.059

cages was quantified by measuring released gas from hydrate samples formed at various CO_2 vapor compositions.

2. Experimental

A schematic diagram and detailed description of the experimental apparatus was given in previous papers [8,10]. The experiment for the equilibrium measurements began by charging the equilibrium cell with about 25 cm^3 of silica gel containing pore water. After the equilibrium cell was pressurized to the desired pressure with a gas mixture of N_2 and CO_2, the cell was cooled slowly to 263 K. When the pressure reduction due to hydrate formation reached a steady-state, the cell temperature was increased at a rate of about 0.1 K/h. The nucleation and dissociation steps were repeated at least two times to reduce possible hysteresis phenomena. The equilibrium pressure and temperature of the three phase (hydrate (H)–water-rich liquid (L_w)–vapor (V)) were determined by tracing the *P–T* profiles from hydrate formation to dissociation. The dissociation equilibrium point in porous silica gel was chosen as the crossing point between the maximum inclination line and the complete dissociation line in the *P–T* profiles. In the present work we tried one equilibrium point several times and finally took a reproducible one. Before we started the experiments associated with gas mixtures, pure CO_2 gas was used to check the equilibrium conditions of pure CO_2 hydrate in both bulk water and 30.0 nm silica gel pores. Also, the reference data for pure CO_2 hydrate in silica gel pores are added and compared with our results.

The H–L_w–V equilibria were measured at four different CO_2 vapor compositions, excluding water content. For composition measurements of gas released from hydrate, a sampling valve with a loop volume of 1 μL was installed and connected to a gas chromatograph on-line, which was previously calibrated for CO_2 and N_2. When the pressure reduction due to hydrate formation reached a steady-state, the vapor phase was removed under vacuum at 243.1 K. Then, the valve was quickly closed to isolate the system, and the temperature was increased to induce complete dissociation of the hydrate phase. The evolving gases were analyzed several times at 272.1 K by a gas chromatograph attached directly to the high pressure cell to eliminate possible errors that might arise during the sampling procedure and to confirm the reproducibility of the data. The composition of released gas from hydrate sample was measured in a range of 3.8 and 85.0 mol% CO_2 to provide the trends of CO_2 composition in hydrate phase. The temperature of cell was measured by a K-type thermocouple probe with a digital thermometer, of which the resolution is ±0.1 K. A Heise tube pressure gauge having the maximum error of ±0.1 bar in the full-scale range was used to measure the cell pressure. The experimental composition deviation for vapor phase was found to be within ±0.1%.

The ^{13}C CP NMR spectra were recorded on a Bruker DSX 400 NMR spectrometer at a Larmor frequency of 100.6 MHz and were used to identify the crystal structure of the mixed hydrate confined in the silica gel pores. The hydrate samples were placed in a 4 mm o.d. Zirconia rotor and were loaded into a variable temperature probe. The pulse length for protons was 5 μs and a pulse repetition delay of 3 s was employed with a contact time of 1.0 ms. 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.

3. Results and discussion

Three-phase H–L_w–V equilibria for ternary CO_2–N_2–water mixtures in 30.0 nm silica gel pores were measured to provide the hydrate formation and dissociation conditions at corresponding vapor phase compositions of 10.0, 17.0, 35.0, and 50.0 mol% CO_2 with the balance N_2, as shown in Fig. 1, which represented the equilibrium conditions of pure CO_2 hydrate formed in both bulk water and dispersed water in 30.0 nm silica gel pores. For comparison, the pore hydrate data reported in the literature [11] were included in Fig. 1 and our data were in good agreement. As can be sufficiently expected, the dissociation pressures of CO_2 hydrate in silica gel pores were shifted to higher pressure region when compared with that in bulk water. Accordingly, it might be worthwhile to note for rational process design that the pores cause the inhibition of hydrate formation similarly to freezing depression due to the addition of salts and alcohols, which results to the reduction of water activity. The H–L_w–V equilibrium pressure of 50.0 mol% CO_2 showed only a small difference compared to that of pure CO_2 hydrate at the corresponding temperatures, but when the composition of CO_2 in the gas mixture decreased below 35 mol% the equilibrium pressure difference became larger shifting to the high pressure region. As expected, CO_2 and N_2 molecules compete with each other for optimum occupancy of the hydrate lattice. Accordingly, the equilibrium conditions for mixed hydrate were influenced by the structure of the mixed hydrate and the distribution of guest molecules over the two types of cages. We used NMR spectroscopic analysis, a well known method for identifying the structural characteristics of gas hydrates [12],

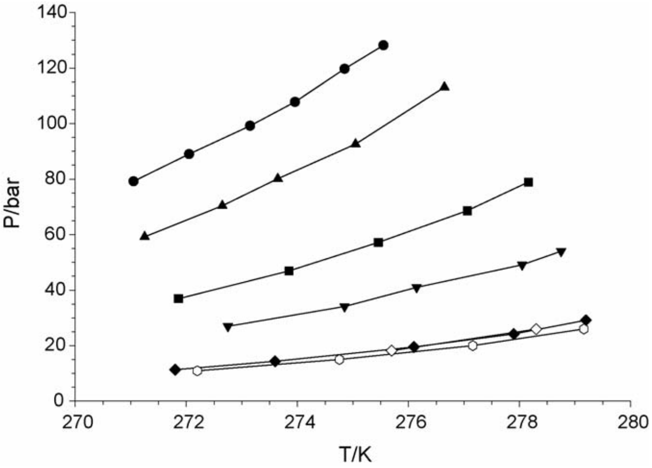

Fig. 1. Hydrate phase equilibria for ternary $N_2 + CO_2$ + water mixtures of various CO_2 compositions in 30.0 nm silica gel pores, and pure CO_2 + water mixture in bulk water: 10 mol% CO_2 (●), 17 mol% CO_2 (▲), 35 mol% CO_2 (■), 50 mol% CO_2 (▼), 100 mol% CO_2 (◆), 100 mol% CO_2 from the results of Uchida et al. [11] (◇), and 100 mol% CO_2 in bulk water (○).

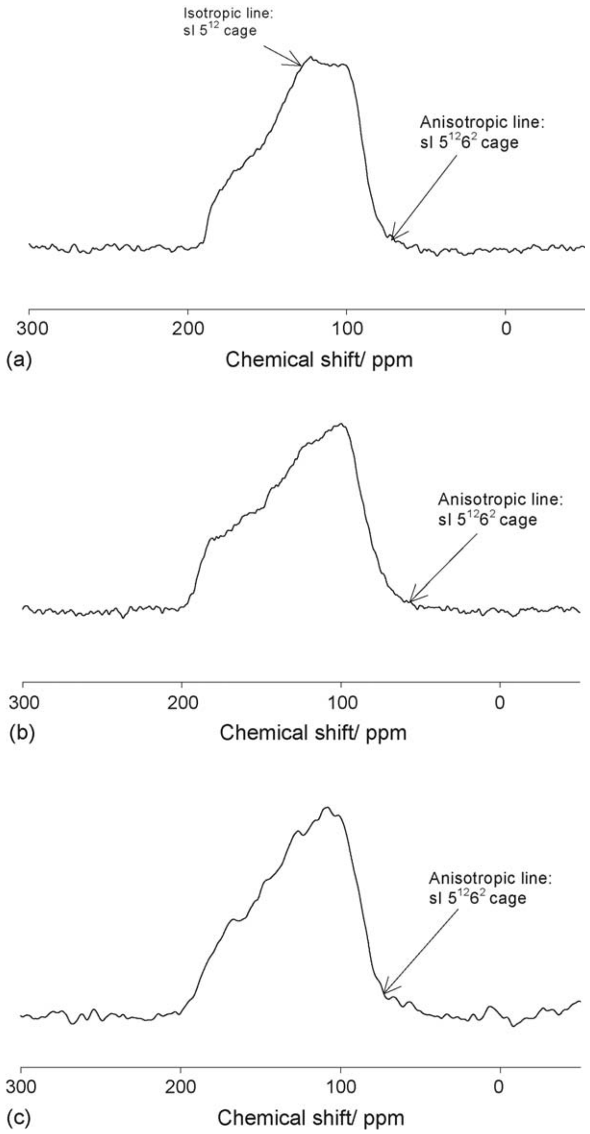

Fig. 2. ^{13}C CP NMR spectra of gas hydrates in silica pores at 243 K. (a) Pure CO_2 hydrate; (b) mixed $N_2 + CO_2$ hydrate formed from 17 mol% CO_2; (c) mixed $N_2 + CO_2$ hydrate formed from 10 mol% CO_2.

and direct gas release measurement were carried out to complement the NMR analysis. Two gas mixture compositions of 10.0 and 17.0 mol% CO_2 were especially chosen to form the mixed hydrate, the compositions being close to that of flue gas. The ^{13}C CP NMR spectra obtained for mixed hydrates are shown in Fig. 2 and compared with that of a pure CO_2 hydrate. Fig. 2a represents the NMR spectrum of pure CO_2 hydrate in silica gel pores. Since the 5^{12} cages of structure I hydrate have pseudospherical symmetry, the molecular motion is isotropic [13], and only a sharp line is observed at the isotropic chemical shift of 123.1 ppm. The broad peak superimposed on the isotropic line represents the anisotropic motions of CO_2 molecules in $5^{12}6^2$ cages of structure I, which are known to have an asymmetric shape (oblate spheroid). These NMR results are in good agreement with the other literature on the bulk hydrate [13,14] and suggest that the structure of gas hydrate confined in silica gel pores is identical to that of the bulk hydrate. The ^{13}C NMR spectrum of mixed hydrate formed with 17.0 mol% CO_2, is shown in Fig. 2b. The broad peak reflecting the anisotropic motion of CO_2 molecules in asymmetric $5^{12}6^2$ cages is observed in the range of 100.2–188.5 ppm, however there is no clear isotropic line identifying CO_2 molecules in pseudo-spherical 5^{12} cages. The chemical shift anisotropy can be defined as $\Delta = \delta_{iso} - \delta_{zz}$, where δ_{iso} is the isotropic chemical shift and δ_{zz} is the zz component of the chemical shift tensor, then the observed chemical shift anisotropy value is −55.3 ppm. This implies that the structure of the mixed hydrate is structure I and CO_2 molecules are distributed only in $5^{12}6^2$ cages when the mixed hydrate was formed at a composition of 17.0 mol% CO_2. Subsequently, the mixed hydrate was formed with 10 mol% CO_2, and the ^{13}C NMR spectrum was obtained. As evident in Fig. 2c the NMR spectrum again showed only the broad peak without an isotropic line with chemical shift anisotropy of −42.2 ppm, suggesting that CO_2 molecules primarily occupy the $5^{12}6^2$ cages of structure I when the mixed hydrate is formed in the range of 10 and 17 mol% CO_2. Recent studies [15] with X-ray diffraction have shown that the mixed hydrate was structure II only below 1.0 mol% CO_2. The present NMR approach provides valuable information on hydrate structure and the distribution of CO_2 molecules in the hydrate cages, however it could not give the exact amount of CO_2 occupying hydrate cages.

The direct measurement of the composition of gas released from mixed hydrates was carried out for various CO_2 vapor compositions. Fig. 3 represents the resulting CO_2 compositions of the hydrate phase at the corresponding compositions of the vapor phase, and shows a trend of increasing CO_2 content in the hydrate with increase of CO_2 in the vapor phase. From the NMR spectroscopy and the powder XRD [15] measurements showing structure I at 10 mol% CO_2 and the increasing composition of CO_2 in hydrate, the structure of mixed hydrate was found to be structure I in gas mixtures containing more than 10 mol% CO_2. Therefore, the distribution of CO_2 molecules in the cages could be evaluated using the ideal occupancy of N_2 and CO_2 molecules in 5^{12} and $5^{12}6^2$ cages ($2N_2{\cdot}6CO_2{\cdot}46H_2O$), resulting

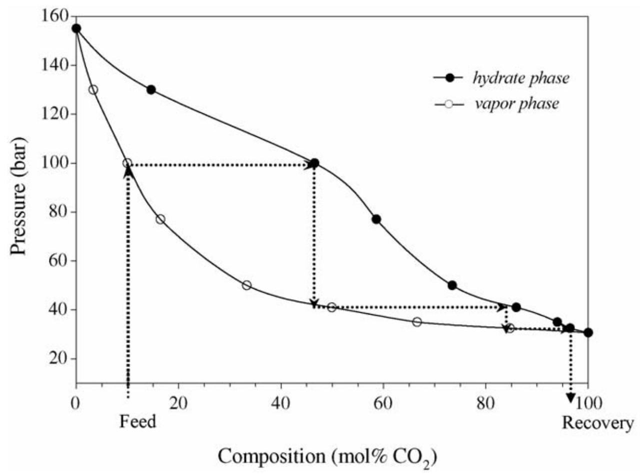

Fig. 3. Pressure–composition diagram of the ternary $N_2 + CO_2$ + water system measured at 272.1 K. The arrow path conceptually illustrates the three-stage recovery process of CO_2 from a binary gas mixture.

in a composition of the hydrate phase of 75.0 mol% CO_2. At a low CO_2 concentration in the vapor phase of 3.8 mol% CO_2, the amount of CO_2 occupying the hydrate cages is 15.2 mol% CO_2. As the amount of CO_2 in the vapor phase increased up to 34.8 mol% CO_2, the CO_2 molecules occupy only part of the $5^{12}6^2$ cages and N_2 molecules occupy the other $5^{12}6^2$ and most of the 5^{12} cages, from the fact that the composition of the hydrate appears to be 46.0, 60.0, and 73.0 mol% CO_2 at corresponding gas compositions of 10.0, 17.0, and 34.8 mol% CO_2, respectively, which are lower than that for the ideal occupancy. However, above 50 mol% CO_2 gas mixture, the composition of hydrate appears to be 87.9, 92.5 and 96.0 mol% CO_2 at corresponding gas compositions of 50.6, 67.0 and 85.0 mol% CO_2, respectively. This implies that CO_2 molecules occupy most of the $5^{12}6^2$ cages and even part of the 5^{12} cages of structure I. With increasing numbers of CO_2 molecules in hydrate cages, the role of stabilizing both small and large cages was transformed from N_2 to CO_2 molecules, which results in the decrease of the hydrate equilibrium pressure at corresponding temperature as shown in Fig. 1. The gas mixture released from this hydrate can be used to form hydrate again and following three cycles of formation and dissociation, a recovery of more than 96 mol% CO_2 in the gas mixture can be achieved, as illustrated in Fig. 3.

4. Conclusions

A further investigation of the effect of the experimental conditions such as temperature and pore size in the silica gel should allow an optimization of both conversion rate and total yield. The combination of thermodynamic analysis and NMR spectroscopy suggests that a higher concentration of CO_2 can be accumulated in hydrate cages via distribution over both 5^{12} and $5^{12}6^2$ cages. On the basis of current experimental results, it is now clear that formation of hydrate in silica gel pores, offers the feasibility of recovering CO_2 from flue gases emitted by power plants although the details of the process still need to be optimized to give improved rates and higher yields. Above all, to meet the scale-up requirements, the hydrate formation reactor must provide enough contact time between flue gas and silica gels containing water in their pores for formation of gas hydrate and needs to be designed for the concentrated gas to be readily collected after dissociation. One of the possible techniques proposed for hydrate reactor might be a series of reactors with the repeated processes of formation and dissociation. The flue gas is injected to the first reactor conditioned for hydrate formation and then contacted with water in silica gel pores to form hydrate. After completing hydrate formation, the first reactor condition is changed to the optimized dissociation one and the flue gas is conveyed to the second reactor for the overall process to be continuous. The required number of reactors is determined from the total volume of flue gas treated in the given time as well as the formation/dissociation kinetic rates. Of course, besides these sufficient conditions, some other important external process variables must be seriously considered during scale-up procedures.

Acknowledgements

This research was performed by the National Research Laboratory (NRL) Program of KOSEF funded by the Ministry of Science and Technology of Korea, and partially supported by the Brain Korea 21 Project.

References

[1] E.D. Sloan, Clathrate Hydrates of Natural Gas, 2nd ed., Marcel Dekker, New York, 1998.

[2] H. Teng, A. Yamasaki, M.K. Chun, H. Lee, Energy 22 (1997) 1111.

[3] P.G. Brewer, G. Friederich, E.T. Peltzer, F.M. Orr Jr., Science 284 (1999) 943.

[4] G.A. Jeffrey, Inclusion Compounds, vol. 1, Academic Press, London, 1984.

[5] T. Uchida, S. Takeya, Y. Kamata, I.Y. Ikeda, J. Nagao, T. Ebinuma, H. Narita, O. Zatsepina, B.A. Buffett, J. Phys. Chem. B 106 (2002) 12426.

[6] S. Subramanian, E.D. Sloan Jr., J. Phys. Chem. B 106 (2002) 4348.

[7] K.A. Udachin, C.I. Ratcliffe, J.A. Ripmeester, Angew. Chem. Int. Ed. 40 (2001) 1303.

[8] Y. Seo, H. Lee, J. Phys. Chem. B. 107 (2003) 889.

[9] S.-P. Kang, H. Lee, Environ. Sci. Technol. 34 (2000) 4397.

[10] Y. Seo, H. Lee, T. Uchida, Langmuir 18 (2002) 9164.

[11] T. Uchida, T. Ebinuma, S. Takeya, J. Nagano, H. Narita, J. Phys. Chem. B 106 (2002) 820.

[12] J.A. Ripmeester, C.I. Ratcliffe, J. Phys. Chem. 92 (1988) 337.

[13] J.A. Ripmeester, C.I. Ratcliffe, Energy Fuels 12 (1998) 197.

[14] K.A. Udachin, C.I. Ratcliffe, J.A. Ripmeester, J. Phys. Chem. B 105 (2001) 4200.

[15] Y.-T. Seo, H. Lee, J. Phys. Chem. B 108 (2004) 530.