Structural transition range of methane-ethane gas hydrates during decomposition below ice point

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04/07/2020

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Hydrate structure



Phase equilibrium curve of methane hydrates



G. Song, Y. Li, W. Wang, S. Liu, X. Wang, Z. Shi, S. Yao, Fuel 2019, 237, 475-485

Structural transition in gas hydrates



Raman spectroscopy

- Determine hydrate structures and structural transition
- Very sensitive to relative sizes of the cage and the guest

Background work

Transformations in methane hydrates



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SCIENTIFIC REPORTS Received: 14 February 2016 Accepted: 14 November 2016 Published: 12 December 2016

OPEN Self-preservation and structural transition of gas hydrates during dissociation below the ice point: an *in situ* study using Raman spectroscopy

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Background work

Time-Resolved in Situ Neutron Diffraction Studies of Gas Hydrate: Transformation of Structure II (sII) to Structure I (sI)

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Received January 31, 2001 J. Am. Chem. Soc. 2001, 123, 12826-12831

Neutron scattering patterns of sII Ar hydrate changes into sI hydrate at 243 K after excess Ar was vented and exchanged with CO2 at 6.21 MPa: (a) Initial sII Ar hydrates at 243 K and 34.5 MPa of Ar; (b) approximately 50% of the sII hydrates converted to sI hydrates within 2 days after the excess Ar was replaced with 6.21 MPa CO2 at 243 K; (c) 95% of the sII hydrates converted to sI hydrates the gas exchange



Motivation



Why this paper?

- 1. They mentioned the dimensions of reactor precisely.
- 2. Raman characterization
- 3. Mechanism of the dissociation



Introduction

- The structural transition of methane-ethane gas hydrates is generally observed during the forming process.
- Study on the dissociation behavior of methane-ethane hydrate below ice point has important implications on gas storage and transportation.
- ➡ The dissociation of a series of methane-ethane hydrate samples at atmospheric pressure and temperatures below ice point (272.15 – 269.15 K) was performed.
- Influence of gas composition and temperature on the structural transition was examined using in situ Raman spectroscopy.
- The mechanism of the structural transition occurring in gas hydrate decomposition was proposed.

Experimental procedures

- ⇒ Firstly, the sample cell was loaded with 0.7 mL of deionized water.
- The HPOC was cooled using a circulating water bath; after the system temperature became stable at 274.15 K, it was maintained for 2 h,
- Then the $CH_4 + C_2H_6$ gas mixture was charged into the cell to a pressure of 3 MPa.



Fig. 1. Schematic diagram of in situ Raman measurements.



Results

Dissociation of methane+ethane hydrate (sl) sample at different temperature and atmospheric pressure

Gas Mixture			Structure		
	269 K	270 K	271 K	272 K	
40 mol% CH ₄ + 60 mol% C ₂ H ₆	×	×	×	×	sl
45 mol% CH ₄ + 55 mol% C ₂ H ₆	×	×	×	×	sl
50 mol% CH ₄ + 50 mol% C ₂ H ₆	~	~	×	×	sll
60 mol% CH ₄ + 40 mol% C ₂ H ₆	~	~	×	×	sll
70 mol% CH ₄ + 30 mol% C ₂ H ₆	×	×	×	×	sll

How to detect the structural change?

Method 1



Hydrate structures transition from sI to sII

Fig. 4. Raman spectra of hydrate formed by 45 mol% CH_4 + 55 mol% C_2H_6 at different times during dissociation at 270.15 K and atmospheric pressure. The peak positions remain unchanged throughout the decomposition process.



Fig. 7. Raman spectra of hydrate formed by $50 \text{ mol}\% \text{ CH}_4 + 50 \text{ mol}\% \text{ C}_2\text{H}_6$ at different times during dissociation at 270.15 K and atmospheric pressure. The peak positions change at 317 min.

Method 1



Fig. 15. Raman spectra of hydrate formed by 70 mol% $CH_4 + 30 \text{ mol}\% C_2H_6$ at different times during dissociation at 270.15 K and atmospheric pressure. For this system, the peak positions remain unchanged throughout the dissociation at the full range of decomposition temperatures (272.15 K-269.15 K).



Pressures of transition: (a) water–sI and water–mixed hydrate of methane + ethane versus ethane concentration in the gas phase at 273 K

Zhdanov, R. K. et al., J ENG THERMOPHYS-RUS. 2010, 19, 282-288

Method 2



Arnaud Desmedt 's Research Homepage

Peak area ratio (PAR) $A_L/A_S = 3$ for sl $A_1/A_s = 0.5$ for sll

 A_L refers to the total area of peaks corresponding to the cavities (5¹²6² for sI or 5¹²6⁴ for sII); A_S refers to the small cavities (5¹²).





Hydrate structures transition from sl to sll



Fig. 9. Individual Raman spectra of hydrate formed by 50 mol% $CH_4 + 50$ mol % C_2H_6 at different times during dissociation at 270.15 K and atmospheric pressure. The values of PAR are higher than 3.0 at the initial stage of decomposition process, with the increase of decomposition time, the values of A_I/A_S are lower than 1.5.



Fig. 14. Individual Raman spectra of hydrate formed by 60 mol% $CH_4 + 40 \mod C_2H_6$ at different times during dissociation at 270.15 K and atmospheric pressure. The peak positions shift to the left; and the hydrate structure transforms from type I to type II.

Methane-ethane hydrate dissociation mechanism



Conclusion

	Gas components	Equilibrium gas components	270.15 K	269.15 K
Run 1 Run 2 Run 3 [41]	$\begin{array}{l} 50 \ mol\% \ CH_4 \ + \ 50 \ mol\% \ C_2H_6 \\ 60 \ mol\% \ CH_4 \ + \ 40 \ mol\% \ C_2H_6 \\ 68 \ mol\% \ CH_4 \ + \ 32 \ mol\% \ C_2H_6 \end{array}$	$\begin{array}{l} 53.8 \ mol\% \ CH_4 \ + \ 46.2 \ mol\% \ C_2H_6 \\ 63.2 \ mol\% \ CH_4 \ + \ 36.8 \ mol\% \ C_2H_6 \\ 72.5 \ mol\% \ CH_4 \ + \ 27.5 \ mol\% \ C_2H_6 \end{array}$	317 ± 56 min 208 ± 48 min 93 ± 30 min	$993 \pm 197 \min 524 \pm 162 \min 67 \pm 99 \min$

Occurrence time of structural transition at different decomposition temperatures and gas components.