

**Supplementary Materials to**  
**“Hydrate phase equilibrium of CH<sub>4</sub>+N<sub>2</sub>+CO<sub>2</sub> gas mixtures and cage**  
**occupancy behaviors”**

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### Figure captions

Figure S1. The mole ratio of CH<sub>4</sub> in large cages and small cages ( $3x/\theta$ ) (calculated by CSMHYD program).

Figure S2. Relationship of values of  $\theta/x$  of N<sub>2</sub> and CO<sub>2</sub> molecules with temperature.

Figure S3. Occupancy ratios of N<sub>2</sub> and CO<sub>2</sub> in hydrate cages (calculated by CSMHYD program).

Figure S4. Mole ratios of N<sub>2</sub>/CO<sub>2</sub> in small and large cages(calculated by CSMHYD program).

Figure S5. Relative occupancies of CH<sub>4</sub>/N<sub>2</sub>/CO<sub>2</sub> in small cages (a), large cages (b) and hydrate cages(c) (calculated by CSMHYD program).

Figure S6. Variation of occupancy of CO<sub>2</sub> in large cages with the concentration of CH<sub>4</sub> in gas phase.

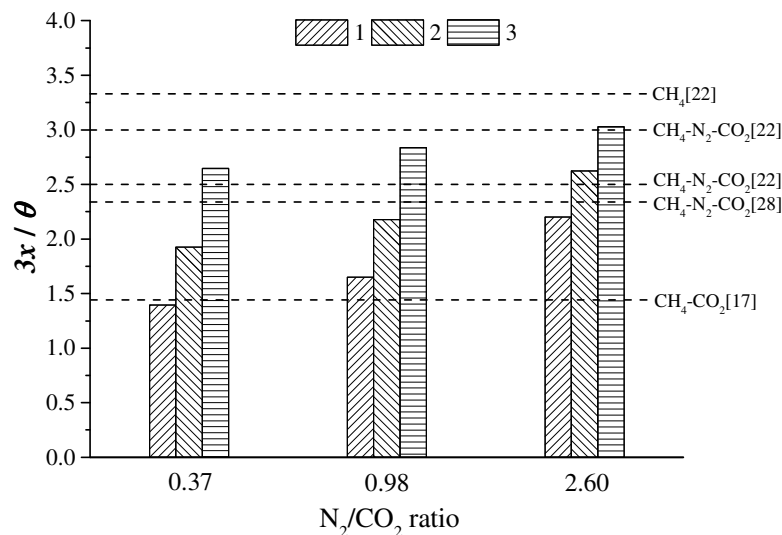


Figure S1. The mole ratio of CH<sub>4</sub> in large cages and small cages ( $3x/\theta$ ) (calculated by CSMHYD program) The numbers of 1, 2 and 3 respectively represent the CH<sub>4</sub> levels of 20%, 50% and 80% in each group with different N<sub>2</sub>/CO<sub>2</sub> ratios.

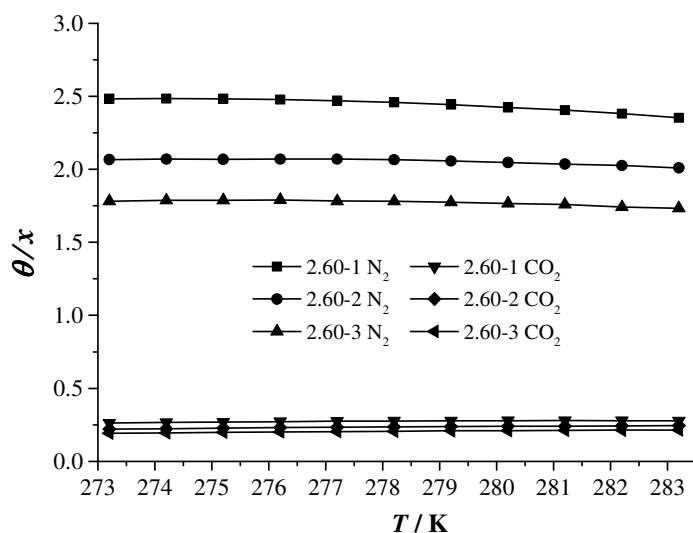


Figure S2. Relationship of values of  $\theta/x$  of N<sub>2</sub> and CO<sub>2</sub> molecules with temperature. The numbers of 1, 2 and 3 respectively represent the CH<sub>4</sub> levels of 20%, 50% and 80% in each group with different N<sub>2</sub>/CO<sub>2</sub> ratios.

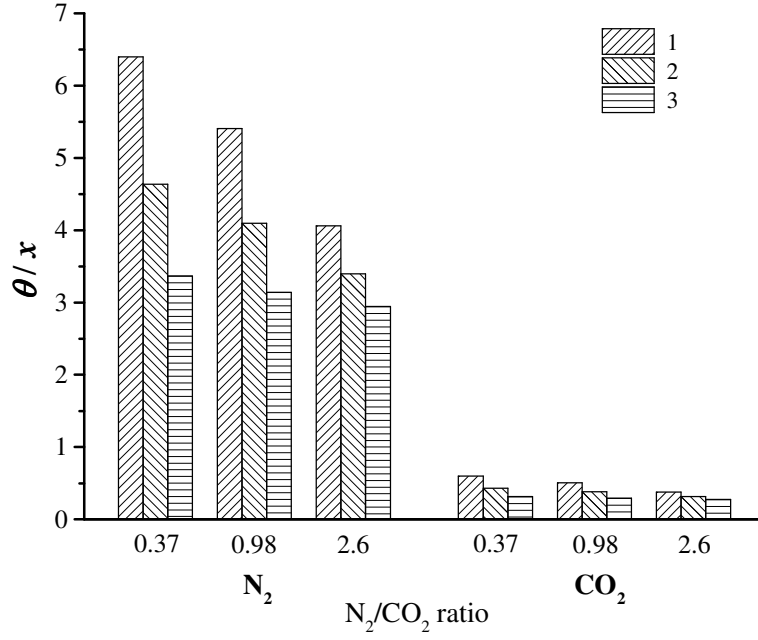
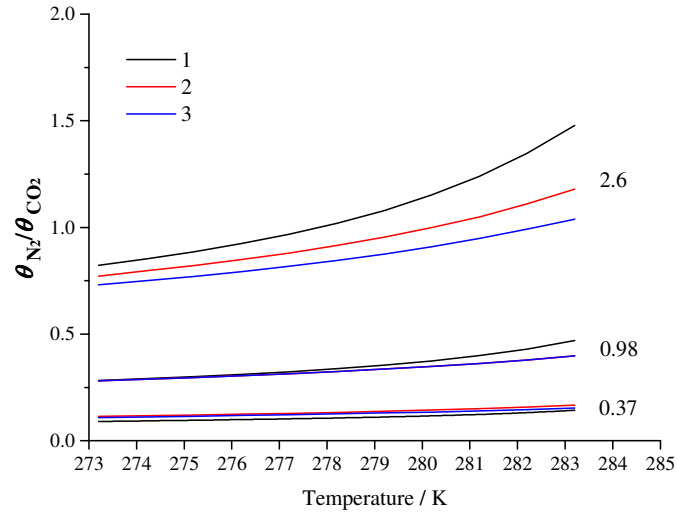
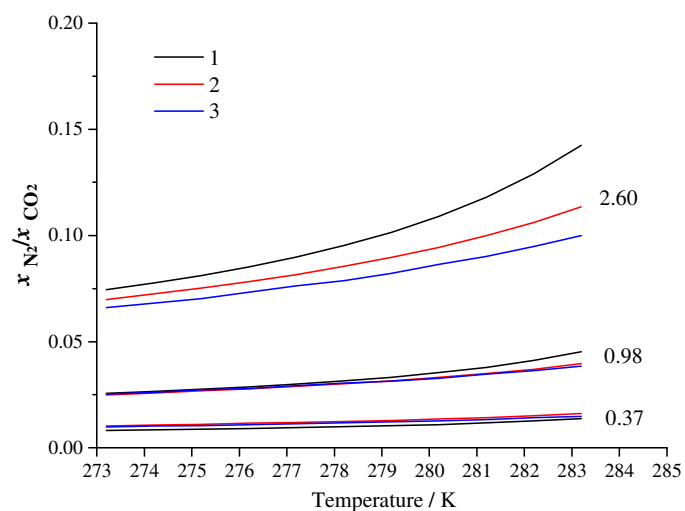


Figure S3. Occupancy ratios of  $N_2$  and  $CO_2$  in hydrate cages (calculated by CSMHYD program). The numbers of 1, 2 and 3 respectively represent the  $CH_4$  levels of 20%, 50% and 80% in each group with different  $N_2/CO_2$  ratios.

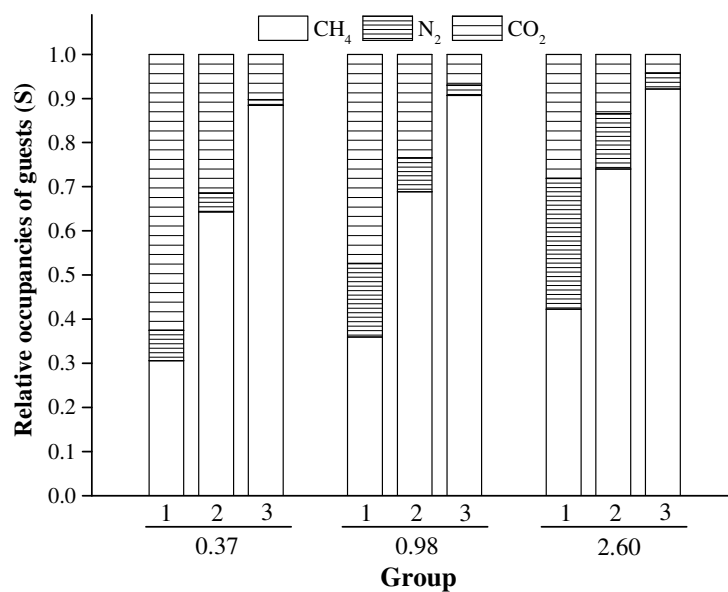


a. In small cage

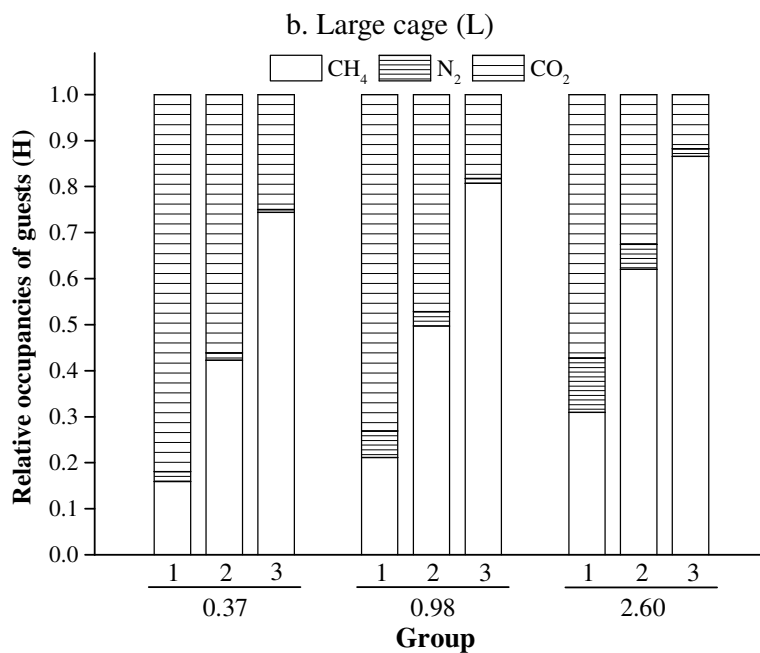
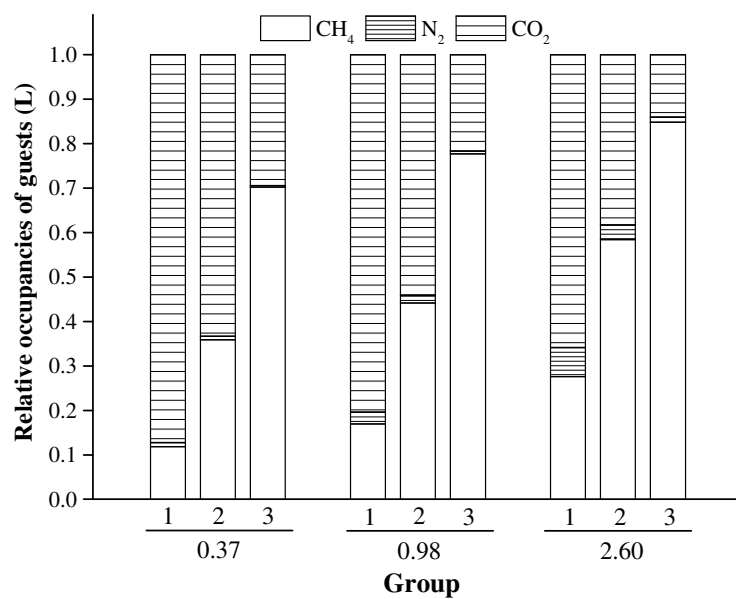


b. In large cage

Figure S4. Mole ratios of  $N_2/CO_2$  in small and large cages (calculated by CSMHYD program). The numbers of 1, 2 and 3 respectively represent the  $CH_4$  levels of 20%, 50% and 80% in each group with different  $N_2/CO_2$  ratios.



a. Small cage (S)



c. Hydrate cages (H)

Figure S5. Relative occupancies of  $\text{CH}_4/\text{N}_2/\text{CO}_2$  in small cages (a), large cages (b) and hydrate cages (c) (calculated by CSMHYD program). The numbers of 1, 2 and 3 respectively represent the  $\text{CH}_4$  levels of 20%, 50% and 80% in each group with different  $\text{N}_2/\text{CO}_2$  ratios.

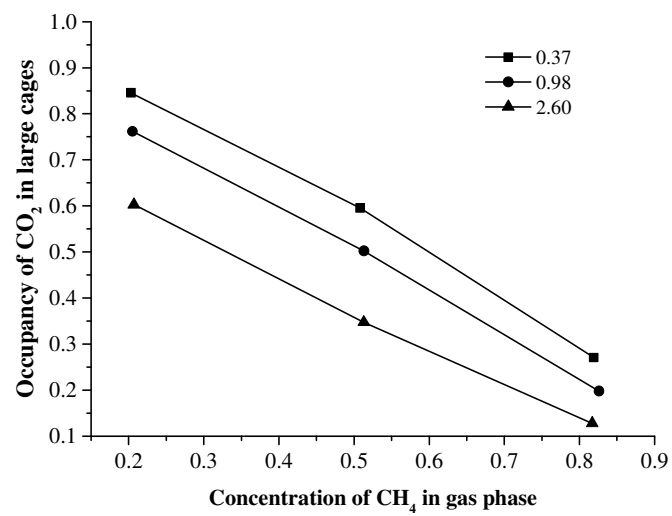


Figure S6. Variation of occupancy of CO<sub>2</sub> in large cages with the concentration of CH<sub>4</sub> in gas phase