Enhanced Methane Recovery from Methane Hydrates Replaced with Mixed Nitrogen and Carbon Dioxide Flue Gas

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In this research, Raman and $^{13}\mathrm{C}$ NMR spectroscopy are used to investigate the structure and distribution of guest molecules of substituted CH $_4$ hydrates with $\mathrm{N_2+CO_2}$ mixed gas and CH $_4$ + $\mathrm{N_2+CO_2}$ mixed hydrates. All the structure of the hydrates in this work are revealed to be structure I hydrate from the NMR results. CH $_4$, $\mathrm{N_2}$ and CO $_2$ guest molecules are all identified in the substituted hydrate sample according to the Raman results. Therefore CH $_4$ in the small and large cages of hydrates are replaced with $\mathrm{N_2}$ and CO $_2$ gas respectively considering the size of guest molecules. From the $^{13}\mathrm{C}$ NMR results, the peaks which indicate CH $_4$ in the small and large cavities independently have not a so great deviation. It means that similar amount of $\mathrm{N_2}$ and CO $_2$ gas occupy the small and large cages of CH $_4$ hydrates. Consequently, the flue gas consisting of mainly $\mathrm{N_2}$ and CO $_2$ can be applied to recover CH $_4$ gas from CH $_4$ hydrate under the deep sea.