Hydrogen storage in tetra n-butyl amonium bromide semi-clathrate hydrates : kinetics and evolution of hydrate phase composition by in situ Raman spectroscopy

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HYDROGEN STORAGE IN TETRA N-BUTYL AMONIUM BROMIDE SEMI-CLATHRATE HYDRATES: KINETICS AND EVOLUTION OF HYDRATE-PHASE COMPOSITION BY *IN SITU* RAMAN SPECTROSCOPY

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In order to elucidate the potential of H_2-TBAB semi-clathrate hydrates for H_2 storage, kinetic data and *in situ* Raman spectroscopy measurements were obtained for two TBAB concentrations (2.6 mol% and 3.7 mol% in the liquid solution) in a pressure range of 5 – 16 MPa. The influence of pressure, TBAB concentration and formation method (T-cycle method and T-constant method) on the hydrate nucleation, hydrate growth and H_2 storage capacity was determined. The results showed that kinetics are favored at higher pressures and solute concentrations. Less stochastic nature was observed when the T-cycle method was applied. The inclusion of H_2 in the semi-hydrate phase was confirmed.

Introduction

Tetrabutylammonium bromide (TBAB) semi-clathrate hydrates, or TBAB semi-hydrates are crystalline inclusion compounds formed by H_2O molecules and by TBAB salts. Recently, TBAB semi-hydrates have been proposed as potential H_2 storage materials [1]. In order to develop semi-hydrate based technology for H_2 storage, it is necessary to take into account the optimal kinetics of formation, which depends on the conditions applied. Therefore, time-dependent experiments were performed in this study in order to determine the optimal formation kinetics as well as the H_2 storage potential of H_2-TBAB semi-hydrates.

Results

The influence of pressure (5-16 MPa), TBAB concentration (2.6 mol% and 3.7 mol%) and formation method (T-cycle method and T-constant method) on the hydrate nucleation, hydrate growth and H_2 storage capacity was determined. The results showed that kinetics are favored at higher pressures and solute concentrations. It was also observed that the H_2-TBAB semi-hydrate formation at constant cooling rate (T-cycle method) exhibited shorter induction times with a less stochastic nature compared to the T-constant method. There was not observed any influence of the formation method on the hydrate growth and amount of H_2 consumed.

Additionally, a new apparatus was built and tested to study the hydrate phase formation and dissociation for a solution of 2.6 mol% of TBAB *in situ* by using the Raman spectroscopy technique. The inclusion of H_2 in the semi-hydrate phase was confirmed. Results showed the importance of H_2 mass transfer on the storage capacity of the H_2-TBAB semi-hydrates.

Conclusions

In order to developed semi-clathrate hydrate based technology for H_2 storage, higher pressures and solute concentrations should be used to assure optimal kinetics. The T-cycle method should be applied to reduce the stochastic nature of the semi-hydrate formation. Finally, to assure optimal H_2 storage, the H_2 mass transfer limitations should be eliminated by means of increasing the contact surface area by the liquid and gas phases or the hydrate and gas phases.

References

[1] Hashimoto S, Murayama S, Sugahara T, Sato H, Ohgaki K. Thermodynamic and Raman spectroscopic studies on H2+tetrahydrofuran+water and H2+ tetra-n-butyl ammonium bromide+water mixtures containing gas hydrates. Chem Eng Sci 2006;61(24):7884-8.

M.Sc. Alondra Torres earned her bachelor degree from Universidad Autonoma del Estado de Mexico and her master degree (cum laude) from Universidad Iberoamericana in Mexico City. Currently Alondra Torres is appointed as a Ph.D. student at Delft University of Technology in the Netherlands. During her studies Alondra Torres has been involved in several projects including; heavy metals removal from waste water with organic material and the formation of polymeric membranes with supercritical CO_2 for gas separation. Her current Ph.D. project involves the study of the potential of clathrate hydrates for hydrogen storage.

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