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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The 6th symposium “Hydrogen & Energy” follows the 5th symposium on 23. – 28. January 2011 in Stoos with more than 80 participants. It serves as an information platform of the fundamental science and technology and the frontiers of research on hydrogen and energy.

The symposium consists of invited keynote lectures reviewing the key elements of the hydrogen cycle, i.e. the hydrogen production, hydrogen storage and hydrogen combustion and fuel cells. Furthermore, contributions on the conversion of renewable energy in general and energy carriers beside and beyond hydrogen are very welcome. The world leading experts present the current research challenges and most important results in invited and contributing talks. Early stage and experienced researchers present their newest results and the open questions on posters as well as in a one slide presentation.

The conference will take place in the conference and wellness hotel Stoos in the beautiful small village Stoos on 1’270 m above see level. The village is free of traffic on a alp above Schwyz in central Switzerland.

The number of participants is limited to 80.


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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 H2-TBAB semi-clathrate hydrates for H2 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 H2 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 H2 in the semi-hydrate phase was confirmed.

Introduction

Tetrabutylammonium bromide (TBAB) semi-clathrate hydrates, or TBAB semi-hydrates are crystalline inclusion compounds formed by H2O molecules and by TBAB salts. Recently, TBAB semi-hydrates have been proposed as potential H2 storage materials [1]. In order to develop semi-hydrate based technology for H2 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 H2 storage potential of H2-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 H2 storage capacity was determined. The results showed that kinetics are favored at higher pressures and solute concentrations. It was also observed that the H2-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 H2 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 H2 in the semi-hydrate phase was confirmed. Results showed the importance of H2 mass transfer on the storage capacity of the H2-TBAB semi-hydrates.

Conclusions

In order to developed semi-clathrate hydrate based technology for H2 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 H2 storage, the H2 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


Alondra Torres

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 CO2 for gas separation. Her current Ph.D. project involves the study of the potential of clathrate hydrates for hydrogen storage.

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