Promoting the Insertion of Molecular Hydrogen in Tetrahydrofuran Hydrate With the Help of Acidic Additives

The Thuong Nguyen, Claire Pétuya, David Talaga, Arnaud Desmedt

To cite this version:
The Thuong Nguyen, Claire Pétuya, David Talaga, Arnaud Desmedt. Promoting the Insertion of Molecular Hydrogen in Tetrahydrofuran Hydrate With the Help of Acidic Additives. Frontiers in Chemistry, Frontiers Media, 2020, 8, 10.3389/fchem.2020.550862. hal-03047184

HAL Id: hal-03047184
https://hal.archives-ouvertes.fr/hal-03047184
Submitted on 8 Dec 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Promoting the Insertion of Molecular Hydrogen in Tetrahydrofuran Hydrate With the Help of Acidic Additives

The Thuong Nguyen¹, Claire Pétuya¹,², David Talaga¹ and Arnaud Desmedt¹*

¹ Groupe Spectroscopie Moléculaire, ISM, UMR5255 CNRS—University, Bordeaux, France, ² Jet Propulsion Laboratory, California Institute of Technology, Passadena, CA, United States

Among hydrogen storage materials, hydrogen hydrates have received a particular attention over the last decades. The pure hydrogen hydrate is generated only at extremely high-pressure (few thousands of bars) and the formation conditions are known to be softened by co-including guest molecules such as tetrahydrofuran (THF). Since this discovery, there have been considerable efforts to optimize the storage capacities in hydrates through the variability of the formation condition, of the cage occupancy, of the chemical composition or of the hydrate structure (ranging from clathrate to semi-clathrate). In addition to this issue, the hydrogen insertion mechanism plays also a crucial role not only at a fundamental level, but also in view of potential applications. This paper aims at studying the molecular hydrogen diffusion in the THF hydrate by in-situ confocal Raman microspectroscopy and imaging, and at investigating the impact of strong acid onto this diffusive process. This study represents the first report to shed light on hydrogen diffusion in acidic THF-H₂ hydrate. Integrating the present result with those from previous experimental investigations, it is shown that the hydrogen insertion in the THF hydrate is optimum for a pressure of ca. 55 bar at 270 K. Moreover, the co-inclusion of perchloric acid (with concentration as low as 1 acidic molecules per 136 water molecules) lead to promote the molecular hydrogen insertion within the hydrate structure. The hydrogen diffusion coefficient—measured at 270 K and 200 bar—is improved by a factor of 2 thanks to the acidic additive.

Keywords: strong acid, hydrogen storage, tetrahydrofuran, hydrates, clathrates, Raman spectroscopy

INTRODUCTION

Hydrogen is the most abundant element on Earth and is considered as a clean and potential energy vector in the future. H₂ storage and transportation are the subject of numerous studies. Among gas storage materials, hydrogen clathrate hydrates (also called hydrates) have received a particular attention over the last decades (Florusse et al., 2004; Veluswamy et al., 2014). Gas hydrates are crystalline inclusion compounds of hydrogen bonded water molecules forming cages encapsulating guest molecules (Sloan and Koh, 2008; Broseta et al., 2017; Ruffine et al., 2018). The pure H₂ clathrate hydrate is generated only at extremely high-pressure (few thousands of bars) and at low temperature (~240 K) (Dyadin et al., 1999; Mao et al., 2002). The hydrate is then formed with H₂ molecular species located in the small cages (SC) and in the large cages (LC) of the so-called sII hydrate (consisting of 16 SCs and 8 LCs) (Mao et al., 2002). To enable the storage of H₂ under softer conditions (typically 50 bars and 280 K), the method consists in co-including H₂ molecules...
with a second guest such as tetrahydrofuran (THF), to form a mixed THF-H$_2$ sII hydrate (Florusse et al., 2004; Lee et al., 2005). However, THF molecules occupy the LC and H$_2$ molecules are only in the SC, which leads to low hydrogen storage (<2 wt%) (Strobel et al., 2006; Mulder et al., 2008) and limits the potential applications (Nakayama et al., 2010). Since this discovery, there have been considerable efforts to optimize the storage capacities of H$_2$ in clathrate hydrates through the variability of the formation condition, of the cage occupancy, of the chemical composition (by changing the promoter and its concentration) or of the cage structure (from clathrate to semi-clathrate) (Veluswamy et al., 2014).

Beyond the problematic of H$_2$ storage capacity for potential applications, the H$_2$ insertion mechanism plays is of fundamental interest. When H$_2$ gas pressure is applied onto a powdered THF hydrate, the formation mechanism involves two steps: hydrogen adsorption onto the clathrate particle surface, followed by subsequent diffusion of hydrogen into the clathrate hydrate particle. The inter-cage diffusion represents the limiting step (timescale of the order of days), involving high activation energy (78.7 kJ/mol) (Nagai et al., 2008), confirmed by electronic structure calculations (Alavi and Ripmeester, 2007). To improve the storage capability of H$_2$ in hydrates, one issue concerns the possibility of modifying the water cage relaxation. The dynamic properties of various hydrates have been investigated and water molecules reorient on a millisecond timescale (Sloan and Koh, 2008). Recently, it has been shown that water molecules relax on a nanosecond timescale in strong acid clathrate hydrates (Desmedt et al., 2004, 2013; Bedouret et al., 2014). Moreover, THF clathrate hydrate may be prepared by co-including strong acid molecules (Desmedt et al., 2015). Such chemical modification has an impact onto the lattice dynamics of the cages and on the melting points of the hydrates (Desmedt et al., 2015). However, to the best of our knowledge, no studies have been performed until now to investigate the H$_2$ storage in such THF clathrate hydrates co-including strong acid species.

The description of the H$_2$ insertion mechanism outlines the key role played by dynamical processes met in clathrate hydrates (Desmedt et al., 2012, 2017). At atmospheric pressure, only intra-cage diffusion of H$_2$ is experimentally observed in the THF-H$_2$ hydrate stability region (i.e., below ca. 270 K) (Pefoute et al., 2012). At higher pressure (typically several tens of bars), studies of molecular hydrogen diffusion into THF hydrates have been performed by means of NMR method (Okuchi and Koh, 2007), in situ neutron diffraction (Mulder et al., 2008), volumetric measurements (Nagai et al., 2008), theoretical calculations (Alavi and Ripmeester, 2007) and molecular dynamics simulations (Cao et al., 2013). These measurements, performed in various P-T thermodynamics conditions, lead to diffusion coefficient ranging from ca. $10^{-6}$ cm$^2$/s to ca. $10^{-12}$ cm$^2$/s. These results outline the importance of using an experimental method allowing the direct investigation of the spatial and time characteristics of the H$_2$ diffusion within the hydrate. In this issue, confocal Raman microspectroscopy is a non-destructive approach and is particularly adapted for in situ investigation of transport process in nanoporous systems (Marti-Rujas et al., 2004, 2006, 2007). This vibrational technique is an interesting label-free tool to access the molecular composition, the molecular selectivity, the structural and dynamical information in gas hydrates (Chazallon et al., 2017; Petuya et al., 2017, 2018a,b; Petuya and Desmedt, 2019). Raman spectroscopy has been performed to study the hydrogen storage in hydrates (Florusse et al., 2004; Ogata et al., 2008; Strobel et al., 2009; Grim et al., 2012) and it has been shown that THF hydrates may act as a molecular sieving for hydrogen-containing gas mixtures (Zhong et al., 2017). This paper aims at studying the H$_2$ diffusion mechanism in the THF clathratehydrate by in situ confocal Raman microspectroscopy and imaging, and at investigating the impact of strong acid onto this diffusive process at 200 bar pressure. To address this issue, we use two different sII hydrogen hydrate formed with THF promoter: THF-H$_2$ hydrate (non-acidic) and the THF-HClO$_4$-H$_2$ hydrate (acidic).

**EXPERIMENTAL DETAILS**

**Samples**

Two solutions were prepared with the following molar ratio 8THF-136H$_2$O (melting at 277 K) and 7THF-1HClO$_4$-136H$_2$O (melting at 271 K) using ultra-pure water (Milli-Q quality) and commercially available chemicals (70% HClO$_4$ aequous solution and 99.9% THF from Sigma-Aldrich). They were transferred under inert atmosphere in the lab-made high-pressure optical cell used for the Raman spectroscopic analysis. According to a procedure previously published (Desmedt et al., 2015), the hydrates have been formed under stirring conditions by cooling the sample temperature to 270 K and maintaining this temperature for 24 h with the help of a modified cryogenic stage (Linkam Scientific Instruments Ltd., UK). Once the hydrate is formed, hydrogen gas (99.9999% Air Liquide) was then applied at constant pressure (200 bar) with a PM High Pressure pump (Top Industrie, Vaux-le-Penil, France) which contains 100 cm$^3$ of gas.

**Raman Scattering and Imaging**

Raman data were collected with a Labram microspectrometer (Horiba Jobin Yvon, Villeneuve d’Ascq, France) and using a 514 nm laser source (10 mW power at the sample). A 50X objective (NA = 0.45, Olympus) permitted to focus the incident laser beam and to collect the Raman scattering. The Raman scattering was dispersed with a holographic grating of 1,800 g/mm and analyzed with a Peltier-cooled CCD detector (Andor, Belfast, UK), which permitted to measure the Raman spectra with a spectral resolution of 1 cm$^{-1}$. The data was collected on a spectral range from 2,700 to 4,300 cm$^{-1}$ to monitor the hydrogen stretching modes. To probe the H$_2$ diffusion into the preformed hydrate as a function of time, micro-Raman spectra and imaging were collected in situ under the 200 bar H$_2$ pressure at 270 K in the hydrate stability zone (Hashimoto et al., 2007). The measurement has been started simultaneously with the application of H$_2$ pressure (corresponding to time $t = 0$ h in the following). For recording the spectral images, a motorized stage was used to map the sample in a point-by-point mode using a 20 µm step size in the two XZ plane perpendicular to the gas-hydrate interface contained in the XY plane (Figure 1). For each
sample, an area of about 200 × 1,200 µm² from the H₂/hydrate interface to 1,000 µm depths in the hydrate by Raman micro-imaging. In the following, Z = 0 µm corresponds to the gas-hydrate interface. Raman intensity depth profiles of inserted H₂ were corrected from the refraction by using standard procedure (Everall, 2000; Desmedt et al., 2007) with a refraction index n = 1.33 (Sloan and Koh, 2008) for the hydrate.

RESULTS AND DISCUSSION

In the present investigation, two hydrates have been considered: the THF hydrate (formed with a THF-17H₂O solution) and the mixed THF-HClO₄ hydrate (formed with a 0.875THF-0.125HClO₄·17H₂O solution). In these II hydrates, the SCs are empty to welcome H₂ molecules, the THF molecules occupy the
LC and the acidic additive HClO$_4$ is inserted within the LC by replacing one THF per unit cell in average (Desmedt et al., 2015). The insertion of molecular hydrogen within these two preformed hydrates has been probed thanks to real-time Raman imaging. An example of the spectral region corresponding to the gaseous H$_2$ and confined H$_2$ signatures is shown in Figure 1A for the THF-H$_2$ hydrate formed within the lab-made high-pressure optical cell after 1 day at 200 bars and 270 K. The rotation-vibration coupled bands of gaseous H$_2$ are observed at 4,130, 4,147, 4,155, and 4,164 cm$^{-1}$. In the case of the THF-H$_2$ hydrate, the band at 4,130 cm$^{-1}$ is assigned to the Raman signal of H$_2$ confined in the sII hydrate SCs (Ogata et al., 2008; Strobel et al., 2009; Grim et al., 2012). To monitor the insertion of hydrogen within the hydrate, Raman imaging has been performed in the plane perpendicular to the gas/hydrate interface (see Figure 1B). An example of visualization of the H$_2$ molecules confined in the hydrate is shown in Figure 1C through the Raman mapping of the ratio of the band intensity at 4,130 cm$^{-1}$ and of the one at 4,155 cm$^{-1}$. The Raman intensity being proportional to the encapsulated species concentration (Zhong et al., 2017), such a Raman image is a direct signature of the spatial H$_2$ distribution within the preformed THF hydrate; after 1 day of pressurization, one can observe that H$_2$ has mainly been inserted within few tens of micrometers below the hydrate surface. In order to spatially analyse the extension of H$_2$ insertion, one needs to locate the gas/hydrate interface at a micrometric scale. In this purpose, the intensity profiles of the H$_2$ vibron and of the OH stretching modes have been measured with the help of
the projection of the acquired Raman spectra in the XZ plane along the Z axis (see Figure 1B). An example of such averaged profiles is shown in Figure 2 (left) for the measurement at initial stage \((t = 0\) h) of \(\text{H}_2\) pressurization at 200 bar and at \(T = 270\) K. A pseudo-Voigt function has been used to reproduce the experimental data of the OH integrated intensity profile and the H\(_2\) intensity profile has been fitted with a sigmoidal function. The fitted functions reproduce with a good agreement the experimental data (the residual error between experimental and modeled curves reached a value of \(10^{-3}\)). The gas/hydrate interface is then clearly identified at the intersection of these two curves: it corresponds to the Z coordinate of the inflection point of the H\(_2\) sigmoidal curve. This procedure allows to accurately determine the Z position of the gas/hydrate interface and is set as the reference distance \(Z = 0\) m. Moreover, the H\(_2\) vibrion intensity profile can be used as a signature of the H\(_2\) diffusion front position as a function of time. This is shown in Figure 2 (right): the H\(_2\) intensity profiles of THF-HClO\(_4\)-H\(_2\) hydrate after 12 h of pressurization is clearly Z-shifted with respect to the profile at initial time \(t = 0\) h. This Z difference of the H\(_2\) diffusion front is the signature of the insertion of H\(_2\) molecule within the hydrate sample; it is defined as the mean H\(_2\) diffusion length, \(\Delta Z(t)\):

\[
\langle \Delta Z(t) \rangle = Z(t) - Z(0)
\]

where \(Z(t)\) corresponds to the inflection point of the H\(_2\) sigmoidal curve at time \(t\). To subsequently analyse the time-evolution of the \(\text{H}_2\) insertion, such \(\text{H}_2\) Raman intensity profiles have been recorded every 12 h over a period of 3 days. In order to evaluate the impact of the strong acid HClO\(_4\) additive, these measurements have been performed onto the preformed THF hydrate and onto the preformed THF-HClO\(_4\) hydrate, both pressurized with H\(_2\) gas at 270 K and 200 bar. The time evolution of the H\(_2\) intensity profiles is shown in Figure 3 for the THF-HClO\(_4\)-H\(_2\) hydrate and for the THF-H\(_2\) hydrate. It can be observed a marked difference between these time evolutions: the H\(_2\) diffusion front extend over a wider range in the case of the THF-HClO\(_4\) hydrates compared to the case of the THF hydrate, i.e., without acidic additives. In order to quantitatively analyse the time evolution of the H\(_2\) diffusion front within the hydrates, each intensity profile has been fitted by using the sigmoidal function as previous described, allowing to measure the position of the H\(_2\) diffusion front as a function of time. Such procedure allows to measure the H\(_2\) diffusion lengths (Equation 1) as a function of time. Their mean-squared values \(\langle \Delta Z(t)^2 \rangle\) are reported in Figure 4. These curves show clearly the improvement of the H\(_2\) insertion when acidic additive are included in the THF hydrate: the values are higher for the THF-HClO\(_4\) hydrate than for the THF-H\(_2\) hydrate.

Furthermore, such curves provide the opportunity to investigate the H\(_2\) insertion mechanism. Such diffusive mechanism may include various elementary processes including the inter-cage diffusion and possible contributions associated with grain boundaries and structural defects. Let first consider two principal diffusive models by analogy with nanoporous systems (Marti-Rujas et al., 2007): conventional diffusion or single-file-like diffusion. The conventional diffusion corresponds to the Fick law for which the mean-squared H\(_2\) diffusion length is given by the Einstein diffusion model in a three-dimensional system:

\[
\langle \Delta Z(t)^2 \rangle = 6Dt
\]

where \(D\) is the H\(_2\) diffusion coefficient. The Fick behavior may reproduce not only the inter-cage diffusion, but also the diffusion associated with grain boundaries and structural defects. The single-file-like diffusive model may be considered for the H\(_2\) inter-cage diffusion. Indeed, the H\(_2\) molecule dimension is

![Figure 4](image-url)
comparable to the diameter of the polygonal faces of the water cages. In such a model, H₂ molecule diffusion within a water cage may proceed under the condition that there is a vacant guest site in the neighboring cage—unlike in the case of Fick behavior for which H₂ molecules can overtake each other in the cages. This phenomenon involves correlations between the H₂ displacements within the hydrate and thus the time-dependence of \( \langle \Delta Z(t)^2 \rangle \) differs from the Fick diffusion:

\[
\langle \Delta Z(t)^2 \rangle = 6Mt^{1/2}
\]

where \( M \) correspond to the H₂ mobility in the three-dimensional hydrate system. The time dependence of \( \langle \Delta Z(t)^2 \rangle \) exhibit a clear linear behavior (it has not been possible to reproduce the experimental data with the single-file-like model). It thus implies that H₂ molecules can overtake each other in a cage and mainly follows a fick behavior. such a diffusive behavior is in full agreement with NMR (Okuchi et al., 2007), \textit{in situ} neutron diffraction (Mulder et al., 2008), volumetric measurements (Nagai et al., 2008), Raman (Zhong et al., 2017), and molecular dynamics (Cao et al., 2013). The Fick law given by Equation (2) have been fitted to the experimental data with an excellent agreement (see \textbf{Figure 4}-Left). The fitted diffusion coefficients are of \( 7.98 \pm 0.03 \times 10^{-11} \text{ cm}^2/\text{s} \) for the THF hydrate and \( 1.46 \pm 0.03 \times 10^{-10} \text{ cm}^2/\text{s} \) for the THF-HClO₄ hydrate at 270 K and 200 bar. The obtained diffusion coefficient for the H₂ insertion in the THF-H₂ hydrate is within the broad range of values obtained by various experimental methods and reported in \textbf{Figure 4}-Right. The present study confirms the trend of an optimum pressure for promoting the hydrogen diffusion at ca. 55 bar. Such a behavior reflects a trend regarding the transport of hydrogen molecules between the cages: the inter-cage diffusion is slower when a large fraction of the small cage is already filled, or even doubly filled with H₂ as reported from Molecular Dynamics simulations (Cao et al., 2013). Once the small cage of the sII THF hydrate are filled, structural or chemical defects and grain boundaries should play a key-role for insuring the Fickian H₂ diffusion through and within the sII THF hydrate. Indeed, the behavior observed with the THF-HClO₄ hydrate confirms the importance of such defects: a clear quantitative enhancement of the H₂ diffusion in the THF hydrate is measured thanks to the co-inclusion of HClO₄ in the sII structure (\textbf{Figure 4}-Left). As reported in previous studies (Desmedt et al., 2015), the inclusion of HClO₄ into the THF hydrate lead to generate perchlorate anions confined in the LC and acidic protons delocalized within the water cage structure (this delocalization is at the origin of the super-protonic conductivity met in strong acid hydrates; Desmedt et al., 2004, 2013). In such a case, the cages are constituted not only of water molecules, but also of hydronium ions. The energy barrier related to H₂ molecules diffusion through the water cage being higher for SC than for LC (Okuchi et al., 2007), the inclusion of such ionic defects in the hydrate lead to modify the flexibility of the cage, as reported from Raman measurements of the water cage phonons (Desmedt et al., 2015). This increased flexibility of the water cage—especially of the SCs welcoming the H₂—may lead to decrease the energy barrier required for an H₂ molecule to cross the faces of the water cage and thus to facilitate the inter-cage diffusion, as reflected by the enhanced diffusion coefficient measured in the THF-HClO₄.

**CONCLUSION**

The present investigation represents the first report to shed light on the impact of ionic defects onto the hydrogen insertion within hydrate. This study has been realized by comparing the H₂ diffusion within the THF hydrate and the mixed THF-HClO₄ hydrate, both being sII structure. Raman confocal microspectroscopy and imaging has been a powerful tool. It yields the measurement of the H₂ Fickian diffusion coefficients within the two hydrates at 270 K and 200 bar: \( 7.98 \pm 0.03 \times 10^{-11} \text{ cm}^2/\text{s} \) for the THF hydrate and \( 1.46 \pm 0.03 \times 10^{-10} \text{ cm}^2/\text{s} \) for the THF-HClO₄ hydrate. In the case of the THF hydrate, it is shown that the H₂ diffusion within the hydrate is optimum for a pressure of ca. 55 bar by compiling this result with those from the literature. Moreover, this investigation clearly shows the enhancement of the H₂ insertion within the THF hydrate thanks to the co-inclusion of acidic additive: it acts as a “flexibilizer” of the water cage through the addition of chemical water H-bond defects (Desmedt et al., 2015) promoting the H₂ inter-cage diffusion. Such results are particularly exciting and promising for applications in storage of hydrogen and open new routes for developing efficient hydrate-based hydrogen storage materials with new type of promoter.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article SUPPLEMENTARY material, further inquiries can be directed to the corresponding author/s.

**AUTHOR CONTRIBUTIONS**

TN and CP have performed the sample preparation, the Raman scattering experiments, and data acquisition. DT has contributed to the Raman spectrometer configuration and data management. TN and AD has analyzed, interpreted the data, and has written the manuscript. All authors contributed to the article and approved the submitted version.

**FUNDING**

This work falls in the frame of the project ANR 2011-JS08-002-01, funded by the French ANR Agence Nationale de la Recherche. The Raman scattering experiments have been performed on equipment of the Vibrational Spectroscopy and Imaging platform (SIV at ISM), funded by the Conseil Régional de Nouvelle Aquitaine and Europe (FEDER programme).
REFERENCES

Alavi, S., and Ripmeester, J. A. (2007). Hydrogen-gas migration through clathrate hydrate cages. *Angew. Chem. Int. Ed.* 46, 6102–6105. doi: 10.1002/anie.200709224

Bedouret, L., Judeinstein, P., Ollivier, J., Combet, J., and Desmedt, A. (2014). Proton diffusion in the hexafluorosulfonic acid clathrate hydrate. *J. Phys. Chem. B* 118, 13337–13364. doi: 10.1021/jp504128m

Broseta, D., Ruffine, L., and Desmedt, A. (2017). *Gas Hydrates 1: Fundamentals, Characterization and Modeling.* London: Wiley–ISTE.

Cao, H., English, N. J., and MacElroy, J. M. D. (2013). Diffusive hydrogen intercage migration in hydrogen and hydrogen-tetrahydrofuran clathrate hydrates. *J. Chem. Phys.* 138:094507. doi: 10.1021/jp4079346

Chazallon, B., Noble, J., and Desmedt, A. (2017). “Spectroscopy of gas hydrates: from fundamental aspects to chemical engineering, geophysical and astrophysics applications,” in *Gas Hydrates 1: Fundamentals, Characterization and Modeling*, eds D. Broseta, L. Ruffine, and A. Desmedt (London, UK: Wiley–ISTE), 63–112.

Desmedt, A., Bedouret, L., Ollivier, J., and Petuya, C. (2017). *Neutron scattering in porous tetrahydrofuran clathrate hydrate.* *Chem. Phys. B* 110, 10708–10713. doi: 10.1016/j.jpcb.2017.06.038

Mulder, F. M., Wagemaker, M., van Eijck, L., and Kearley, G. J. (2008). Hydrogen in porous tetrahydrofuran clathrate hydrate. *Chem. Phys. Chem.* 9, 1331–1337. doi: 10.1002/cphc.200700833

Nagai, Y., Yoshioka, H., Ota, M., Sato, Y., Inomata, H., Smith, J. R., et al. (2008). Binary hydrogen-tetrahydrofuran clathrate hydrate formation kinetics and models. *AIChE J.* 54, 3007–3016. doi: 10.1002/aic.11587

Nakayama, T., Tomura, S., Ozaki, M., and Mori, H. M. (2010). Engineering investigation of hydrogen storage in the form of clathrate hydrates: conceptual design of hydrate production plants. *Energy Fuels* 24, 2576–2588. doi: 10.1021/ef901003a

Ogata, K., Hashimoto, S., Sugahara, T., Moritoki, S., Sato, H., and Ohgaki, K. (2008). Storage capacity of hydrogen in tetrahydrofuran hydrate. *Chem. Eng. Sci.* 63, 5714–5718. doi: 10.1016/j.ces.2008.08.018

Okuchi, T., Moudrakovski, I. L., and Rimpeester, J. A. (2007). Efficient storage of hydrogen fuel in leaky cages of clathrate hydrate. *Appl. Phys. Lett.* 91:171903. doi: 10.1063/1.2802041

Pefoute, E., Kemner, E., Soetens, J. C., Russina, M., and Desmedt, A. (2012). Diffusive motions of molecular hydrogen confined in THF clathrate hydrate. *J. Phys. Chem. C* 116, 16823–16829. doi: 10.1021/jp308656x

Pefoute, C., Damay, F., Chazallon, B., Brunee, J. L., and Desmedt, A. (2018a). Guest partitioning and metastability of the nitrogen gas hydrate. *J. Phys. Chem. C* 122, 566–573. doi: 10.1021/acs.jpcc.7b04151

Pefoute, C., Damay, F., Desplanche, S., Talaga, D., and Desmedt, A. (2018b). Selective trapping of CO2 gas and cage occupancy in CO2–N2 and CO2–CO mixed gas hydrates. *Chem. Commun.* 54, 4290–4293. doi: 10.1039/C8CC0538A

Peyot, C., Damay, F., Talaga, D., and Desmedt, A. (2017). Guest partitioning in carbon monoxide hydrate by raman spectroscopy. *J. Phys. Chem. C* 121, 13798–13802. doi: 10.1021/acs.jpcc.7b04497

Pefoute, C., and Desmedt, A. (2019). Revealing CO-preferential encapsulation in the mixe CO2–N2 clathrate hydrate. *J. Phys. Chem. C* 123, 4871–4878. doi: 10.1021/acs.jpcc.8b011680

Ruffine, L., Broseta, D., and Desmedt, A. (2018). *Gas Hydrates 2: Geoscience Issues and Potential Industrial Applications.* London: Wiley–ISTE.

Sloan, E. D., and Koh, C. A. (2008). *Clathrate Hydrates of Natural Gases.* Boca Raton, FL: CRC Press.

Strobel, T. A., Sloan, E. D., and Koh, C. A. (2009). Raman spectroscopic studies of hydrogen clathrate hydrates. *J. Phys. Chem. C* 113, 10415–10426. doi: 10.1021/jp9016608

Sloan, E. D., Koh, C. A., Miller, K. T., et al. (2006). Molecular hydrogen occupancy in binary THF–H2 clathrate hydrates by high resolution neutron diffraction. *J. Phys. Chem. B* 110, 14024–14027. doi: 10.1021/jp062139n

Veluswamy, H. P., Kumar, R., and Linga, P. (2014). Hydrogen storage in clathrate hydrates: current state of the art and future directions. *Appl. Energy.* 122, 112–132. doi: 10.1016/j.apenergy.2014.01.063

Zhong, J. R., Chen, L. T., Liu, T. C., Zeng, X. Y., Sun, Y. F., Sun, C. Y., et al. (2017). Sieving of hydrogen-containing gas mixtures with tetrahydrofuran hydrate. *J. Phys. Chem. C* 121, 27882–27889. doi: 10.1021/acs.jpcc.7b08945

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Copyright © 2020 Nguyen, Petuya, Talaga and Desmedt. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.

Nguyen et al.

Hydrogen Insertion Promotion in Hydrates