

Application of the β -form hydroquinone clathrate to methane storage and transportation

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In this study, hydroquinone is selected as a possible organic material to be used for storing and transporting methane. This chemical is known to have capturing ability of various molecules while changing its crystal structure to the β -form from its original structure, α -form at high pressures. Formed α - and β -form clathrate samples were analyzed by means of spectroscopic measurements in order to identify cage occupancy and formed crystal structure. Even though the cage occupancy of CH_4 in the β -form hydroquinone is obtained to be 0.8, more investigations are necessary in order to the suggested technique more viable.

1. Introduction

Clathrate compounds have complex structures where one chemical substance ("host") forms cavities into which a "guest" substance is entrapped so as to stabilize the entire crystal structure. In particular, gas hydrates refer to clathrate compounds formed by host water molecules and low molecular-weight guests, while a lot of organic chemicals have also been known to act as host molecules to form organic clathrates. For such organic clathrates, formations of a variety of host and guest species have been reported over a wide range of temperature and pressure conditions. Among various organic

clathrate formers, hydroquinone is known to exist in three crystalline structures, designated as α -, β - and γ -forms (Atwood et al., 1984). In the rhombohedral α -form, hydroquinone is assembled to form hydrogen-bonded double helices and spherical cages, where small guest molecules such as He and Ne can be enclathrated (Mock et al., 1961). The crystal structure of the β -form is also built up from hydrogen bonding between hydroquinone molecules in such a way to form two interpenetrated networks. In the resulting spherical cageworks, volatile guest species such as Ar, Kr, Xe, SO₂, CH₄, and methanol are clathrated via attractive forces (Palin and Powell, 1945; Palin and Powell, 1947; van der Waals and Platteeuw, 1959). The molar ratio of hydroquinone to cages expected for the α -form is 18:1, whereas it is 3:1 for the β -form. The cages in both structures are connected to form 1D channels along the hexagonal *c*-axis, resulting in facile intercage diffusion. At ambient conditions, the α -form is the most stable compared to the β - and γ -forms. A recent study of molecular dynamic simulations, however, indicates that hydrogen-loaded β -hydroquinone clathrates can be stabilized (Daschbach et al., 2006), possibly by loading the metastable empty structure at low temperature.

In this study, hydroquinone is converted into the β -form by reacting with CH₄ gas at 12.0 MPa and room temperature. In addition, obtained β -form samples were collected and analyzed by means of spectroscopic methods such as synchrotron X-ray powder diffraction and solid-state nuclear magnetic resonance (NMR). Experimental results showed that cage occupancy of CH₄ in the β -form cages is around 0.8.

2. Experimental methods

Pure hydroquinone (α -form) with nominal purity of 99 mol% was supplied by Sigma-Aldrich Chemicals Co., and CH₄ gas with minimum purity of 99.995 mol% was purchased from World Gas Co. (Korea). The materials were used without further purification or treatment for the present study. In order to synthesize the CH₄-loaded β -form hydroquinone compound, pure hydroquinone was allowed to react with CH₄ gas in a high pressure reactor. The reactor was made from 316 stainless steel and has internal volume of approximately 200 cm³.

Synchrotron X-ray powder diffraction experiments on the α -form and the CH₄-loaded β -form of hydroquinone compounds were performed at the multi-purpose wiggler beamline 5A at Pohang Accelerator Laboratory (PAL). A monochromatic synchrotron beam of 0.6888 Å in wavelength and 200 μm in diameter was provided by a sagittally-focusing monochromator and mirrors. Each diffraction data was measured for 1 min on MAR345 imaging plate. In addition, to identify the crystalline structure of the hydroquinone samples, a Bruker 400 MHz solid-state NMR spectrometer was also used. The NMR spectra were recorded at 298 K by placing the samples in a 4 mm O.D. Zr rotor. All ¹³C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with the magic angle spinning (MAS) at 9 kHz. The down-field carbon resonance peak of adamantane, which was assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference.

3. Results and Discussions

In order to verify the possible application of hydroquinone as storage and transportation media for CH₄ gas, samples were prepared before and after reacting the chemical with high pressure CH₄ at 12.0 MPa. First, both samples were collected and measured synchrotron X-ray powder diffraction, which are presented in Figure 1. As reported, hydroquinone exists as the α -form in its pure state. However, as it reacts with CH₄ and captures CH₄ molecules into its formed cages, the structure is changed into the β -form. As it can be seen in the following figures, obtained diffraction patterns show some differences in peak positions. In addition, as it can be found by comparing measured diffraction pattern for the α -form and calculated peak positions (vertical lines), obtained experimental results show good agreement with the existing literature values.

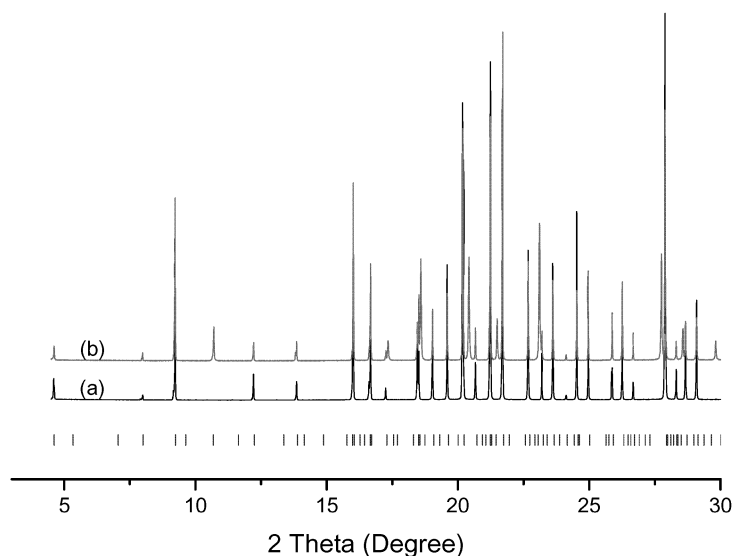


Figure 1. Synchrotron X-ray powder diffraction patterns for (a) the α -form (in pure chemical state) and (b) the β -form of hydroquinone. Vertical lines at the bottom represents calculated peak positions from the literature.

In order to clarify structure changes before and after reaction with CH₄, solid-state NMR spectra were also measured for both samples. As it can be seen in the following figure, ¹³C signal splitting coming from two atomic states of hydroquinone slowly disappears. In addition, even though it is not included in the following figure, ¹³C signal for enclathrated CH₄ molecules were observed at up-field region (- 4.32 ppm). This NMR spectrum leads us to conclude that the α -form hydroquinone is completely converted into the β -form by capturing CH₄ molecules in its cages.

Based on the obtained spectroscopic results, the cage occupancy of hydroquinone in the β -form structure was calculated. NMR peak areas show that the occupancy is about 0.5, while X-ray diffraction pattern shows the value can be 0.8. Because the ¹³C NMR peaks

are affected by molecular interactions, it can be thought that calculation based on the X-ray diffraction pattern, rather than the ^{13}C NMR peak area, is more close to the real cage occupancy. Even considering the cage occupancy of 0.8, the molar ratio of hydroquinone to captured CH_4 is expected to 3.75:1 for the β -form, which will show low weight percentage due to large molecular weight of hydroquinone compared with CH_4 gas. Therefore, in order to apply this chemical to storage and transportation of energy gas, more investigations are required to increase the cage occupancy and viability.

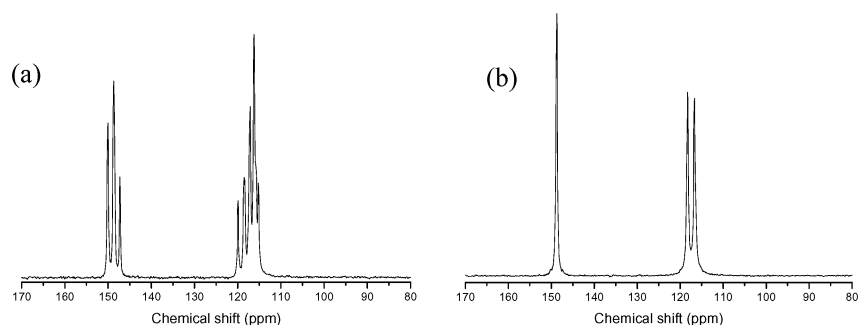


Figure 2. ^{13}C solid-state NMR spectra for (a) the α -form (in pure chemical state) and (b) the β -form of hydroquinone. The right one for the β -form spectrum shows a peak coming from CH_4 molecules captured in the β -form hydroquinone.

4. Conclusion

In this report, hydroquinone is selected as a possible storage and transportation media for CH_4 by forming organic clathrates. Formed hydroquinone samples of the α - and β -forms were collected and measured by means of spectroscopic methods. With synchrotron X-ray powder diffraction and ^{13}C solid-state NMR, structure changes of hydroquinone from the α - to β -form were identified. In addition, the cage occupancy of CH_4 molecules in the β -form structure was calculated to be 0.8. However, in order to increase the viability of hydroquinone as a CH_4 storage and transportation media, more intense works should be performed to significantly increase the storage capacity of CH_4 .

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