

# Methane Storage in Biosilica-Supported Semiclathrates at Ambient Temperature and Pressure

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**Abstract.** Two key issues regarding the use of clathrates and semiclathrates for practical gas storage and transport is the pressure-temperature stability of the material and very low formation kinetics. For many practical applications, the avoidance of cooling, gas overpressure, and mechanical mixing would be very desirable. Here, we show that biosilica supports from rice husks greatly enhance gases uptake kinetics in tetra-iso-amyl ammonium bromide semiclathrates without introducing complex mixing technologies. These systems show excellent thermal stability and good recyclability.

**Keywords:** Semiclathrates; Methane storage; Rice husks; Biosilica.

## 1. Introduction

There is much interest currently in the storage of gases such as methane and carbon dioxide for environmental and energy related application. A wide range of gas storage materials have been investigated, including carbon materials [1], zeolites [2], metal-organic frameworks (MOFs) [3], covalent organic frameworks (COFs) [4], organic crystalline microporous solids & nonporous solids [5], and organic cages [6]. However, few ideal candidates have emerged so far and new strategies are necessary for future breakthroughs [7].

Gas hydrates, also known as gas clathrates, are nonstoichiometric crystalline compounds consisting of hydrogen bonded cages which have potential for gas storage and transport, gas separation, and CO<sub>2</sub> capture [8, 9]. The potential environmental impact of gas hydrates is low because they consist mostly of water, and it has been suggested that it is economically feasible to transport natural gas (methane is main component) in the hydrated form [10]. There are, however, two significant challenges to be addressed before real applications can be achieved: the high pressures and low temperature required for gas hydrates formation and stabilization and the slow kinetics associated with gas enclathration. Concerted efforts have been made to reduce gas hydrates equilibrium pressure by adding thermodynamic promoters. Tetra-hydrofuran (THF) and cyclopentane (CP) are well-known thermodynamic promoters that can significantly lower the required pressure of the clathrate hydrates formation [11, 12]. However, both THF and CP are of volatility and toxicity. By contrast, quaternary ammonium salts (QAS) such as tetra-n-butyl ammonium bromide (TBAB) and tetra-iso-amyl ammonium bromide (TiAAB) are non-volatile and non-toxic and form semiclathrate hydrate with water molecules under atmospheric pressure. AS semiclathrates with guest gases are also more stable to



temperature that other gas hydrates with well-known thermodynamic promoters like THF and CP [13]. Semiclathrates are similar to true clathrates in structures and physical properties. The main difference is that in semiclathrates, quaternary ammonium cations are suited within framework cavities while the anions occupy lattice sites in the hydrogen-bonded framework. Semiclathrates of TBAB have been extensively studied for gas storage and CO<sub>2</sub> capture [14, 15]. However, the reports about semiclathrates of tetra-iso-amyl ammonium (TiAA) salts such as TiAAB are still rarely although they offer a higher thermodynamic stability.

Even if the pressure and clathrate stability issues are successfully addressed, a generic practical limitation may prove to be the kinetics of clathrate formation in the bulk. The gas hydrate formation reaction is an interfacial phenomenon and the rates of hydrate formation have been shown to be inversely proportional to the thickness of the hydrate zone and the surface area of the growing gas hydrate particles. [9] Bulk hydrate formation rates may be extremely slow, and interstitial water is often trapped in the hydrates [16, 17]. Common methods for increasing clathrate formation kinetics - for example, the use of high pressures, vigorous mechanical mixing, surfactants [18], or micron-sized ground / sieved ice particles [19] - can be achieved in the laboratory but may be less cost-effective and practical in the real gas storage application. Here, we investigate the possibility of using silica nanoparticles from eco-friendly and cheap rice husks (RHs) as supports for improving kinetics and recycling gases enclathration within TiAAB semiclathrates without introducing complex mixing technologies.

## 2. Experimental Section

Tetra-iso-amyl ammonium bromide (TiAAB) was synthesized using Menshutkin's reaction [20]. Equimolar amounts of tri-iso-amyl amine (95 %, Chemexcel Zhangjiako Fine Chemicals Co. Ltd.) and iso-amyl bromide (Aladdin, PR China, 96 %) were taken into a three-necked round-bottom flask under an atmosphere of argon. Acetonitrile (99.5%, Aladdin PR China), 15 times the total volume of the reactants, as solvents was then added to the reaction flask. In the original work by Menshutkin, refluxing proceeded for 28 h at 373 K. However, in the current work, refluxing was instead conducted for 72 h at 363 K. This gave a significantly higher yield of TiAAB. The reaction mixture, at room temperature was then extracted three times with petroleum ether at (303 to 330) K to remove mainly the unreacted TiAA. The extracted acetonitrile fraction (containing the desired product TiAAB) was then distilled off and recovered for reuse. The crude residue of TiAAB was then crystallized from ethyl acetate, which was found to be a better solvent than the recommended use of the 2-butanone, with respect to the final yield. The crystallized TiAAB was washed several times with cold ethyl acetate, dried, and weighed.

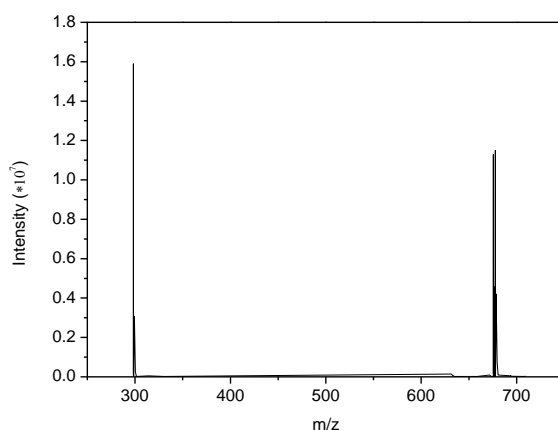
The preparation of biosilica: raw RHs (Guangdong Academy of Agricultural Science) were boiled in 0.2 wt % HCl (37 wt %, Aladdin, PR China) solution for 2 h, rinsed with deionized water, and then dried at 100 °C for 24 h. The dried RHs were then pyrolyzed in a muffle furnace, which was preheated to 700 °C, for 2 h to prepare silica nanoparticles.

To carry out the gas uptake kinetic experiments, 8.0 g of a stock solution of TiAAB·38H<sub>2</sub>O was loaded into a 95.0 cm<sup>3</sup> high pressure stainless steel cell (Kerui Instruments, Gongyi, Henan, PR China) together with the biosilica support (4.0 g). The temperature was controlled by a programmable thermal circulator (DWHW-10, Kerui Instruments, Gongyi, Henan, PR China). The temperature of the compositions in the high pressure cell was measured using a Type K Thermocouple (−250 to 400 °C, Tianyi Cekong, Henan, PR China). The gas pressure was monitored using a High-Accuracy Gauge Pressure Transmitter (0–20 MPa, Tianyi Cekong, Henan, PR China). Both thermocouple and transmitter were connected to a Digital Universal Input Panel Meter (ZNHW, Kerui Instruments, Gongyi, Henan, PR China), which communicates with a computer. Prior to experiments, the cell was slowly purged with gas three times to remove air, and then pressurized to the desired pressure at the designated temperature. The temperature, pressure and time were automatically interval-logged using MeterView 3.0 software (Kerui Instruments, Gongyi, Henan, PR China).

Elemental analyses were performed on a Vario ELIII elemental analysis instrument (Elementar Co.). Mass spectroscopy (MS) was recorded on a Agilent 1100 / Esquire HCT PLUS. Using a Q2000 DSC instrument, a 6.88 mg TiAAB·38H<sub>2</sub>O sample was loaded at 273 K using aluminium sample and reference pans. Data were collected at a heating rate of 1.0 K / min from 273 to 318 K.

### 3. Results and Discussion

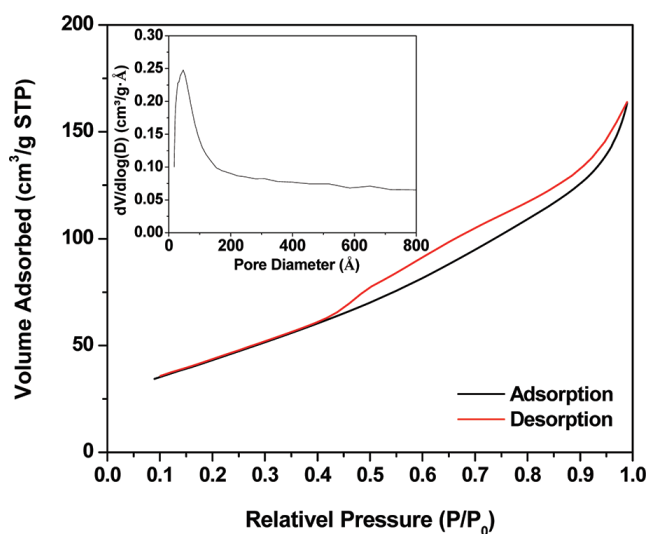
The characterization of TiAAB was performed using mass spectroscopy (MS), and “C”, “H”, and “N” elemental analysis. The results (Fig. 1) from the mass spectroscopy confirm that the reaction product is TiAAB. Table 1 that compares the measured elemental analysis to which is expected from the stoichiometric formula of TiAAB implies that the compound is very pure.



**Figure 1.** Mass spectroscopy results which show the molecular mass of the synthesized TiAAB.

**Table 1.** Elemental Analysis of Synthesized TiAAB

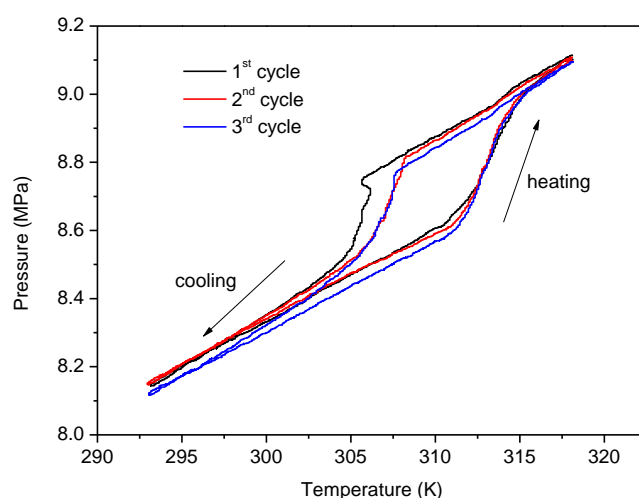
	WC	WH	WN	WBr
Measured	0.634	0.107	0.038	0.221
Theoretical	0.635	0.116	0.037	0.212



**Figure 2.** N<sub>2</sub> sorption isotherms of porous silica nanoparticles. The inset shows the pore size distribution obtained from BJH adsorption.

The surface area characterization (Fig. 2) revealed that biosilica supports have a Brunauer - Emmett - Teller (BET) surface area of 164 m<sup>2</sup>/g. The Barret - Joyner - Halenda (BJH) analysis, as shown in the inset of Fig. 2, revealed that such silica nanoparticles possess pores with a diameter mainly ranging from ca. 2.0 – 9.0 nm.

We next investigated the storage of methane within a TiAAB semiclathrates supported on biosilica mesoporous material. The inter-connected pore structure and very low bulk density allowed us to support 8 g of TiAAB solution on 4 g of the biosilica. Fig. 3 shows a P-T plot for the CH<sub>4</sub> - TiAAB - H<sub>2</sub>O system. With no support, the P-T relationship for CH<sub>4</sub> in the system approximated to the ideal gas law during the heating/cooling cycle (data not shown); that is, very little CH<sub>4</sub> clathrate was formed in the bulk in the absence of mixing. By contrast, clathrate formation and subsequent dissociation occurred in the presence of the biosilica support, as evidenced significant pressure drop on cooling and the pressure rise on heating. On repeating this cycle, the clathration onset temperature increased (308 K versus 305 K in the first cycle). Further repeats of the heating/cooling cycle (up to 30 repeats) then closely follow the second cycle. We speculate that this first “induction cycle” may result from the more uniform distribution of the TiAAB / water system throughout the biosilica support, as discussed previously for polymer-supported TiAAB - H<sub>2</sub>O - CH<sub>4</sub> clathrates. [21] However, it may also arise from the clathrate memory effect that has been reported for a number of different systems. [9] The pressure drop with temperature recovered to a linear trend below 308 K, indicating completion of the CH<sub>4</sub> clathrate formation process. During warming, clathrate dissociation commenced at around 312 K and was completed at 316 K. This shows excellent thermal stability and good recyclability in our systems.

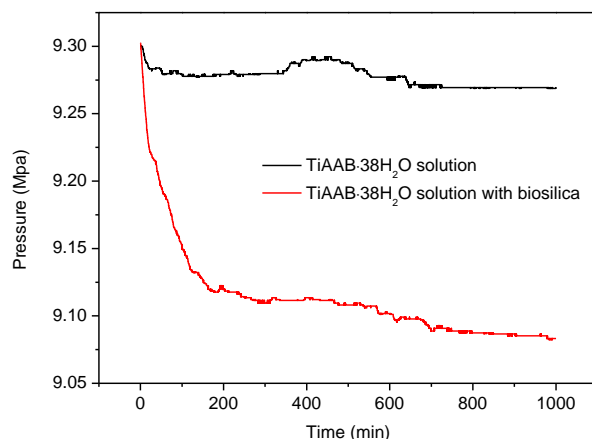


**Figure 3.** P-T plots for biosilica-supported TiAAB·38 H<sub>2</sub>O (8 g solution, 4 g support) during cooling and heating (temperature ramp: 2 K / h).

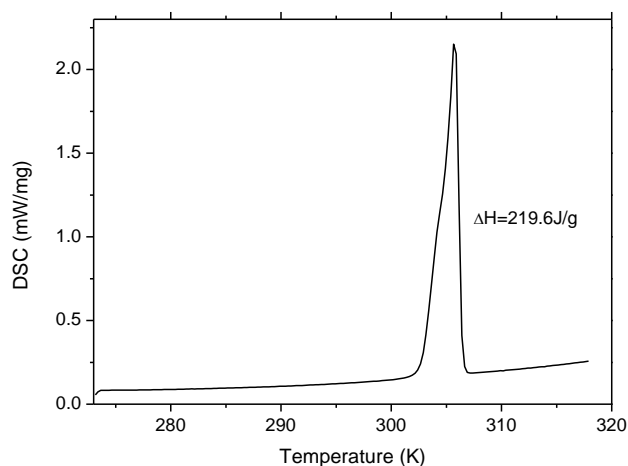
The kinetics of clathration and gas uptake capacity was both greatly enhanced by the presence of the biosilica support (Fig. 4). Again, this effect is reproducible over multiple charge-discharge cycles. The CH<sub>4</sub>-uptake kinetics in the bulk control, experiment curve black), are very slow. A little increase in pressure (around 400 min) is an acceptable error that may result from the temperature fluctuation in the vessel. The use of biosilica as a support, curve red), greatly enhances the CH<sub>4</sub> uptake kinetics. The time to reach 90 % saturation capacity,  $t_{90}$ , was ~ 200 min.

To further examine the thermal stability of the TiAAB-H<sub>2</sub>O clathrate, we used differential scanning calorimetry (DSC) to determine the enthalpies of melting for the TiAAB·38H<sub>2</sub>O clathrate hydrate (Fig. 5). The thermal properties (phase-change temperature, fusion heat) of TiAAB·38H<sub>2</sub>O clathrate hydrate

investigated and analyzed by DSC are 304 K and 219.6 J/g, which illustrate the thermal stability of the TiAAB - H<sub>2</sub>O semiclathrate hydrate, and show its potential as phase change material to storage heat.



**Figure 4.** Kinetic plots for CH<sub>4</sub> encapsulation in TiAAB·38 H<sub>2</sub>O semiclathrates. Red) 8.0 g TiAAB·38 H<sub>2</sub>O solution and 4.0 g biosilica support. Black) 8.0 g TiAAB·38H<sub>2</sub>O solution and 4.0 cm<sup>3</sup> glass beds.



**Figure 5.** Differential scanning calorimetry for TiAAB·38 H<sub>2</sub>O semiclathrate hydrate.

#### 4. Conclusions

In conclusion, we have shown that biosilica supports derived from eco-friendly and easily available rice husks greatly enhance CH<sub>4</sub> uptake kinetics in semiclathrates in the absence of complex mixing technologies. These systems show excellent thermal stability and good recyclability with no degradation in performance over at least 30 charge / discharge cycles. The results may have broader significance in applications such as CO<sub>2</sub> capture, gas separation and heat storage.

#### 5. Acknowledgments

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