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The specific surface area of methane hydrate formed in different conditions and manners

WANG XiuLin[†], SUN ChangYu, CHEN GuangJin, YANG LanYing, MA QingLan, CHEN Jun, TANG XuLong & LIU Peng

State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China

The specific surface area of methane hydrates, formed both in the presence and absence of sodium dodecyl sulfate (SDS) and processed in different manners (stirring, compacting, holding the hydrates at the formation conditions for different periods of time, cooling the hydrates for different periods of time before depressurizing them), was measured under atmospheric pressure and temperatures below ice point. It was found that the specific surface area of hydrate increased with the decreasing temperature. The methane hydrate in the presence of SDS was shown to be of bigger specific surface areas than pure methane hydrates. The experimental results further demonstrated that the manners of forming and processing hydrates affected the specific surface area of hydrate samples. Stirring or compacting made the hydrate become finer and led to a bigger specific surface area.

methane hydrate, the specific surface area, SDS

1 Introduction

Gas hydrates are crystalline compounds formed from water and small gas molecules. There are three known hydrate structures: structure I, structure II and structure H^[1–4]. Recently this ice-like substance has generated more considerable interest as a globally distributed mineral that harbors a significant yet virtually untapped hydrocarbon resource^[5,6]. There are also a lot of researchers interested in developing new technologies based on gas hydrate, e.g., separation of gas mixture by forming/dissociating hydrate^[7–9] and the storage of natural gas in the form of hydrate (NGH)^[10–17], which is appealing for industrial utilization because of its high storage capacity and the storage safety resulting from its higher stability under atmospheric pressure and not very low temperature. Stern et al.^[12] and Shirota et al.^[13] performed methane hydrate dissociation experiments at low temperature, and the results indicated that at 268.2 K, the dissociation percentages within 24 hours and 1 month after dissociation started were 7% and 50%, respectively. Although this so-called self-preservation

phenomenon that gas hydrates are of unexpected stability when they are brought outside their field of thermodynamic stability at temperature below ice point has been observed for decades, the inherent mechanism remains elusive. The ice-shielding mechanism has been taken to be a sound illustration of this phenomenon, in which an ice layer surrounding the hydrate core is assumed to be formed after initial dissociation stage and thickened with the proceeding of hydrates decomposition. The thickening ice layer hinders the hydrate from further decomposition^[18]. Although this mechanism was supported in some extent by a series work done by Takeya et al.^[19], Kuhs et al.^[20] and Tse and Klug^[21]. However, this mechanism can not be used readily to interpret the anomalous characteristic of the self-preservation because the decomposition rates of methane hydrate do

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[†]Corresponding author (email: wangxiucheng1998@163.com)

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not decrease with the decrease of temperature monotonically, which was firstly found by Stern et al.^[12,22,23].

It is well known that the specific surface area of methane hydrates is a very important parameter for the study on the hydrate dissociation rate. But up to now, there are no works reported on the specific surface area of methane hydrates. In this work, the influence of the temperature, the formation manner (stirring or without stirring), the processing manners (compaction or without compaction, holding the hydrate samples for different hours at formation pressures), as well as the formation pressure upon the specific surface were investigated experimentally.

2 Experimental methods

2.1 Equipment and material

A schematic of the experimental apparatus is shown in Figure 1. The critical part of the apparatus is a transparent sapphire cell with a diameter of 2.54 cm through which the formation/decomposition process of the hydrate can be observed directly. The maximum workspace of the cell is 78 cm³, and the designed maximum working pressure is 20 MPa. The volume of the system

can be altered by moving the piston up or down with a hand pump. The change of volume can be read from the scale of the pump with the precision of 0.002 mL. In order to observe the experimental phenomena occurring in the cell clearly, a luminescence source of type LG100H is fixed on the outside of the cell. The system temperature is controlled by an air bath with a precision of 0.1 K. The temperature sensor used is a secondary platinum resistance thermometer (type pt100). A calibrated Heise pressure gauge and differential pressure transducers are used to measure the system pressure with a precision of ± 0.01 MPa. The changes of the system temperature and pressure with time are recorded and displayed by a computer. The apparatus was described in detail in the previous papers published by this laboratory^[24,25].

Analytical grade methane (99.99%) was obtained from Beijing Beifen Gas Industry Corporation. The SDS surfactant with an A.R. grade was purchased from Beijing Yili Fine Chemical Co., Ltd. Distilled water was used to prepare all the solutions. Both weights of water and SDS were weighed by a balance with the precision of 0.1 mg when preparing the SDS aqueous solutions.

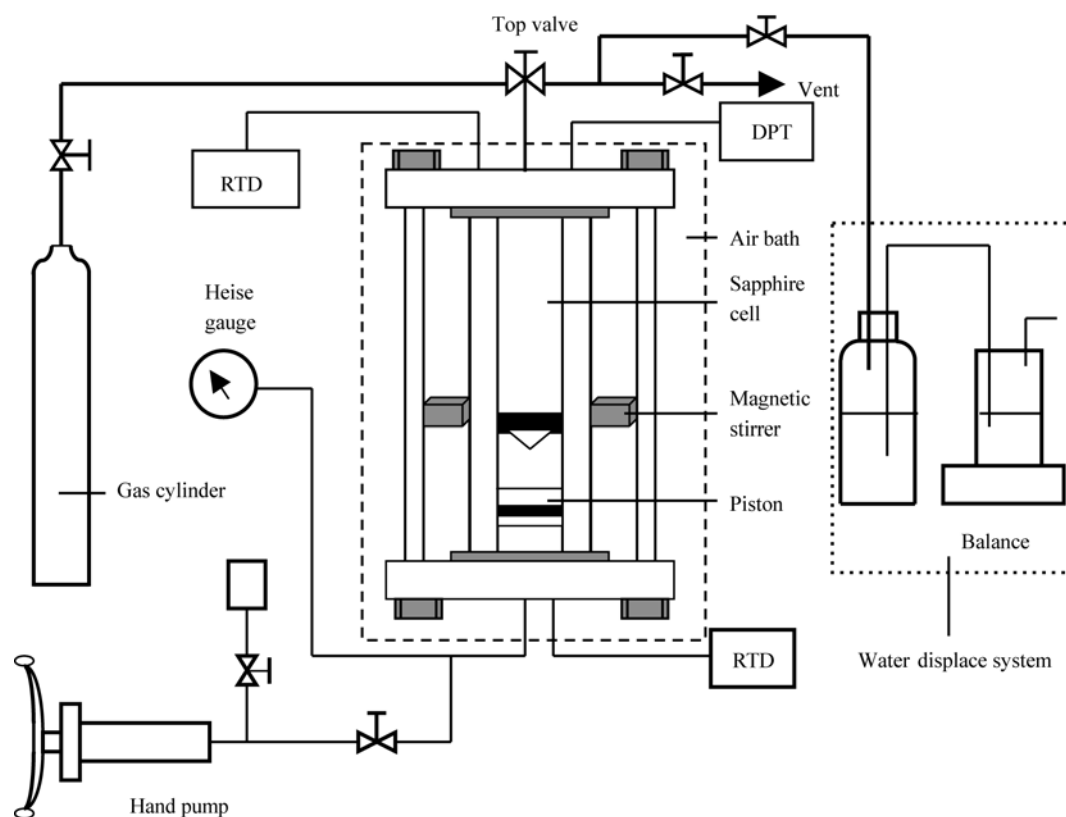


Figure 1 Experimental apparatus for studying the hydrate formation/decomposition phenomenon.

2.2 Preparation of hydrate samples

Before the experiments, the sapphire cell was washed with distilled water and dried. It was then loaded with 10 mL of water or SDS aqueous solutions, which were weighed using the balance. After that, the system was evacuated for about half an hour and the gas space of the system was then purged with methane 4–5 times to ensure the absence of air.

The temperature of the air bath was then adjusted for the desired value at which the hydrate sample was formed. Once the temperature of the system was kept constant, methane was charged into the cell until the system pressure reached the specified value. The stirrer was turned on to speed up the hydrate formation for some groups of experiments. However, for other groups of experiments, the stirrer was not placed in the sapphire cell in order to investigate the influence of the stirring upon specific surface area.

Afterwards, the hydrate samples were processed in different manners before the specific surface area measurement, which will be described in the following section.

2.3 Measurement of specific surface areas of hydrate

In order to measure specific surface area of hydrate, a suitable quantity of the formed hydrate was sampled and put into a glass tube, which was pre-cooled in liquid nitrogen (77 K) before sampling and put back into liquid nitrogen again soon after the sampling. Specific surface area measurements of hydrate samples were performed on a surface area and porosity analyzer, ASAP 2020, made by Micromeritics Corporation, USA. During the measurement, the glass tube with hydrate sample was cooled in liquid nitrogen to avoid the decomposition of the hydrate. The Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area.

3 Results and discussion

3.1 Influence of the presence of SDS

A series of experiments were performed in order to determine the influence of the presence of SDS upon the specific surface area. The experiments were divided into two groups. In the first group, the hydrate samples were formed with stirring, compacted soon after the completion of formation by moving the piston upwards, then cooled down to the desired temperature and held 8 h at that temperature with a fluctuation less than 0.1 K. In

the second group, except for stirring, hydrate samples were formed and handled in the same way as in the first group, i.e., they were formed quiescently, compacted soon after its formation by moving the piston upwards, then cooled down to the desired temperature and held 8 h at that temperature with a fluctuation less than 0.1 K. The effect of SDS on the formation and storage capacity of methane hydrate was studied by Lin et al.^[24]. Their experimental results showed that the optimum SDS concentration and formation temperature were 650 mg/L and 276.4 K corresponding to the maximum hydrate storage capacity (170 v/v)^[24]. Therefore, the hydrate samples for this set of experiments were formed at this optimum condition and 7.0 MPa.

Nitrogen adsorption-desorption isotherm at 77 K of methane hydrates formed with stirring at 276.4 K and 7.0 MPa with/without the presence of 650 mg/L SDS were shown in Figures 2 and 3, respectively. The determined specific surface areas of hydrate samples formed in the absence and presence of SDS are 0.3344 m²/g and 0.8374 m²/g, respectively. This result proves the arguments that the presence of SDS may make the size of hydrate particles become smaller or change the shape of hydrate samples. The specific area becomes bigger and subsequently leads to the increase in the hydrate dissociation rate. As a surfactant, SDS molecules may be adsorbed on the surface of formed hydrate particles and therefore inhibit the growth of hydrate particles into larger ones.

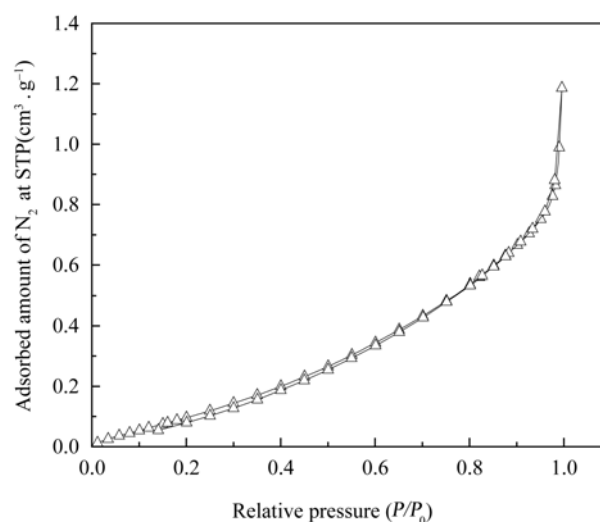


Figure 2 Nitrogen adsorption-desorption isotherm at 77 K of methane hydrates formed with stirring at 276.4 K and 7.0 MPa in the presence of 650 mg/L SDS, cooled at 268.15 K for 8 h.

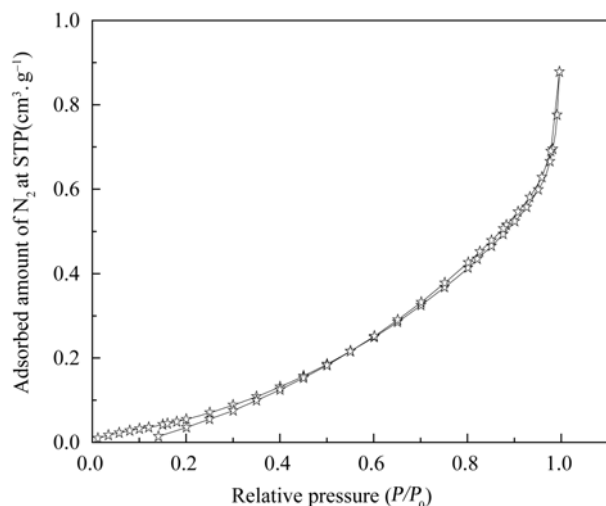


Figure 3 Nitrogen adsorption-desorption isotherm at 77 K of methane hydrates formed from pure water with stirring at 276.4 K and 7.0 MPa, cooled at 268.15 K for 8 h.

The measured specific surface areas of hydrate sample formed in stirring and quiescent conditions in the presence of 650 mg/L SDS were 0.8374 m²/g and 0.6135 m²/g, respectively. The surface area of hydrate sample formed with stirring is bigger than that formed in the quiescent condition. This difference might imply that the stirring inhibited the growth of hydrate particle in size. Thus the average size of hydrate particle was smaller and total dissociation area was bigger correspondingly.

In order to investigate the mechanism of the anomalous preservation behavior of methane hydrate, the specific surface areas of hydrate samples which were formed at the same condition but cooled at different temperatures were measured and showed in Figure 4. As shown in this figure, the specific surface area of methane hydrate increases with the decreasing temperature. We think that the dissociation rate of hydrate always decreases with the decreasing temperature if specific surface area is fixed. It is the increase in the specific surface area that leads to the apparent dissociation rate increasing with the decreasing temperature in some temperature ranges. This might be why the anomalous preservation behavior of methane hydrate occurs.

3.2 Influence of formation pressure

The influence of formation pressure upon the specific surface areas was studied. The hydrate samples used for measuring specific surface areas were formed quiescently, compacted soon after its formation by moving

the piston upwards, cooled down to 268.2 K and held 8 h at that temperature with a fluctuation less than 0.1 K. The formation conditions were specified to 276.4 K and 650 mg/L SDS initial aqueous solution but two different pressures 6.0 and 7.0 MPa.

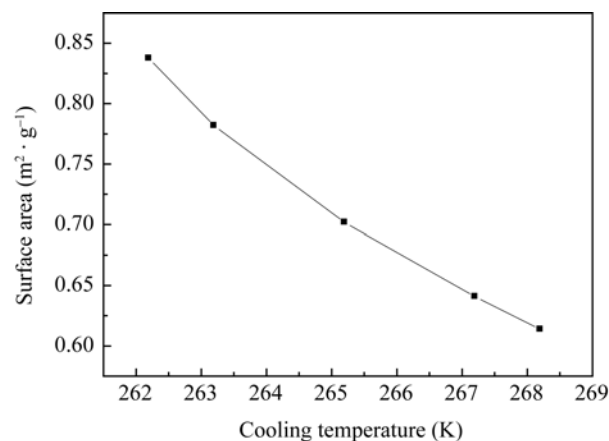


Figure 4 Variation of the hydrate specific surface area with cooling temperature, where methane hydrates were formed quiescently at 276.4 K and 7.0 MPa in the presence of 650 mg/L SDS, cooled at different temperatures for 8 h.

The specific surface areas of hydrate samples formed at 6.0 MPa and 7.0 MPa are measured to be 0.6979 m²/g and 0.6135 m²/g, respectively. It is demonstrated that higher pressure is favorable to form larger hydrate particles and therefore leads to lower dissociation rate of hydrate.

3.3 Influence of compaction

The compaction to hydrate is certainly necessary in industrial application in order to reduce the storage volume. Therefore, the effect of compaction on the specific surface areas was studied, where the hydrate samples were generated quiescently at 276.4 K and 7.0 MPa, cooled 8 h at 268.2 K. The hydrate samples were compacted at 12.0 MPa for 30 minutes by pushing the piston upwards continuously. The surface areas of hydrate samples with compaction and without compaction are measured to be 0.8536 m²/g and 0.6135 m²/g, respectively. It implies that the compaction makes larger hydrate particles into smaller ones and therefore increases the total dissociation area.

3.4 Influence of cooling time

The hydrate samples were formed quiescently at 276.4 K, 7.0 MPa and 650 mg/L SDS in initial aqueous solution, compacted and cooled down to 268.2 K soon after the completion of hydrate formation. The hydrate sam-

ples were held at 268.2 K for different hours in order to investigate the influence of the length of cooling time upon the specific surface area. The variation of the hydrate specific surface area with the cooling time is depicted in Figure 5. It is shown that the specific surface area decreases with the increasing cooling time. Hydrate samples may be accumulated with increasing the length of cooling times. So the specific surface area decreases with the increasing cooling times.

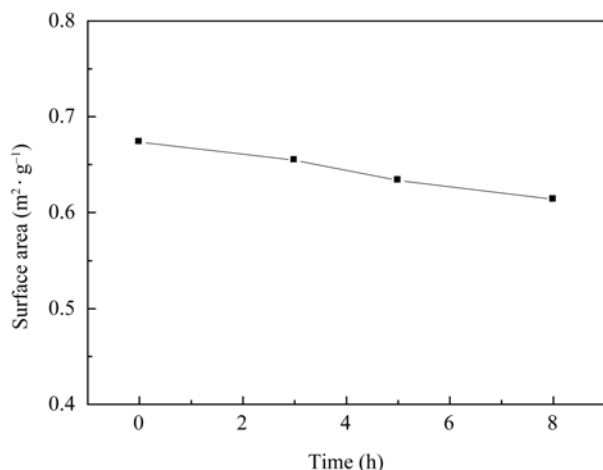


Figure 5 Variation of the specific surface area of methane hydrate in the presence of SDS with the length of cooling time, where hydrate samples were formed quiescently at 276.4 K and 7.0 MPa in the presence of 650 mg/L SDS in water, then cooled down to 268.15 K and held at that temperature for different hours.

3.5 Influence of holding time at formation temperature

In order to further investigate possible agglomeration among hydrate particles, the hydrate samples, which were formed quiescently at 276.4 K and 7.0 MPa in the presence of 650 mg/L SDS in initial aqueous solution, compacted soon after the completion of formation, held at 276.4 K and 7.0 MPa for different hours, cooled down to 268.2 K and held at that temperature for 8 hours.

Figure 6 shows the variation of hydrate specific surface area with the holding time. The tendency that spe-

cific surface area decreases with the increasing holding time is very clear. The results further prove the existence of agglomeration among hydrate particles, therefore the average size of hydrate particles increases with the increasing holding time, and then the specific surface area decreases.

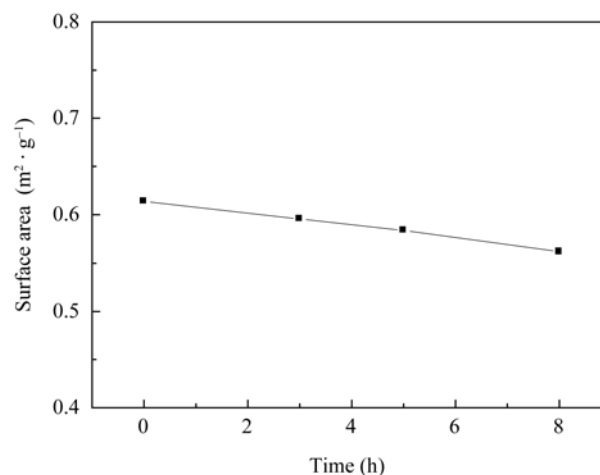


Figure 6 Variation of the specific surface area of methane hydrate in the presence of SDS with the length of holding time, where hydrate samples were formed quiescently at 276.4 K and 7.0 MPa in the presence of 650 mg/L SDS, then held at the formation condition for different hours before being cooled down to 268.2 K and held at that temperature for 8 h.

4 Conclusions

A series of experiments on the specific surface area of methane hydrates both in the presence and absence of SDS, were performed at atmospheric pressure and temperatures below ice point. The influence of conditions and the manners of forming and processing hydrate samples on the specific surface area of methane hydrates were checked systematically. The measurement results showed that the specific surface area of hydrate increased with the decreasing temperature, which might be why anomalous dissociation behavior of methane hydrate occurred. The experimental results further demonstrated that the manners of forming and processing hydrate affected the specific surface area of hydrate samples.

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