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Interfacial effect of cyclodextrin inclusion complex on gas adsorption kinetics of dry water emulsion

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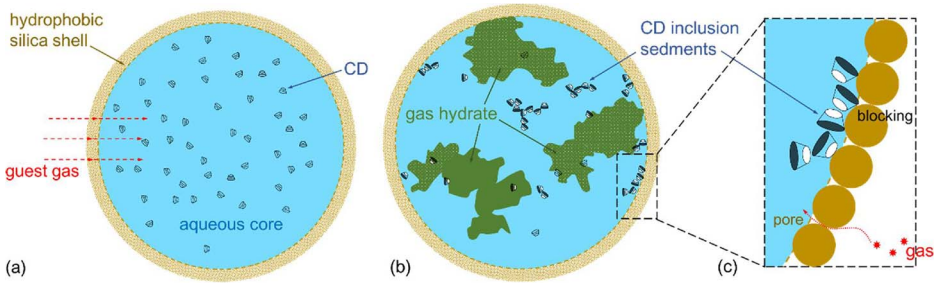
GRAPHICAL ABSTRACT

Schematic diagram of gas adsorption in DW or DCD. (*a*) The initial stage, (*b*) the formation of hydrate and CD inclusion complex, and (*c*) blocking process by CD inclusion sediments.



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ABSTRACT

Cyclodextrins (CD) solutions were mixed with hydrophobic SiO_2 powders to form a dry-cyclodextrin-water (DCD) emulsion, and the effects of CDs with different concentrations and structures on gas adsorption kinetics were investigated, respectively. α-CD was found to enhance effectively both CH_4 and CO_2 gases adsorption capacity of DCD, while β-CD was generally negative to guest gas adsorption with one exception related to CH_4 under lower concentration. Through analyzing dual interfacial effect of gas inclusion, the dominant competition between gas hydration and gas inclusion was speculated as the main reason for the different CD concentration dependence for CH_4 and CO_2 adsorption kinetics. Furthermore, based on considering the cooperative control of gas diffusion, hydration reaction, inclusion reaction and inclusion sedimentation, a diffusion-reaction-blocking model was suggested to describe the kinetic process. CH_4 gases were found to prefer to exist in DCD with free form, while CO_2 gases with adsorption form mainly. The selectiveness closely related to guest gas further illustrated the 'CD concentration quenching' appearing in CO_2 adsorption rather than CH_4 adsorption.

1. Introduction

Recent years have witnessed an ever-growing interest in microcapsules, nanoparticles, and assembled micro/nanostructures due to their special nature. Their benefits for applications have been demonstrated in intracellular delivery, photodynamic therapy and so on [1–3]. As a potential kind of micro/nanostructures self-assembly material, dry water has similar structural characteristics with the above materials, so it has great application potential in many aspects. At present, dry water has also become one of the research spots. Dry Water

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(DW) is a free-flowing powder composed of water droplets, which can be prepared by mixing water with hydrophobic silica nanoparticles at high speed, and the quality of DW is related to the contact angle of silica particles [4]. DW is a water-in-air emulsion actually [5]. In comparison to bulk water and liquid marbles [6], DW has much higher surface-to-volume ratio, which can greatly enhance the kinetics of adsorption in gaseous systems [7,8]. Thus, DW can be considered as a new type of material for gas storage and capture, such as CO_2, CH_4, and Kr [9–11], because the enhanced gas adsorption by their pores between silica particles can also accelerate the hydrate formation process [12]. Nature gas hydrate is considered as a new material for energy storage and transportation, while the formation of CO_2 hydrate is also a possible method to deposit greenhouse gases. At present, improving both the adsorption capacity of DW and the formation rate of gas hydrate within it are still key issues for practical application of DW [13,14].

The first step of hydrate formation is the transport of gas molecules from gas phase to the aqueous phase. A well dispersed water droplet will increase the gas-liquid contact area significantly, leading to an enhanced kinetics of gas hydrate formation [15,16]. Therefore, the usage of DW is expected to improve the gas adsorption kinetics in comparison with bulk water. There are several methods employed to increase the formation rate of hydrates, such as the usage of vigorous mixing devices, the addition of promoting materials (sodium dodecyl sulfate, for example), and the increase of gas-water contact area [17,18]. However, SDS can destroy the structure of DW owing to the decreased surface tension, and then the gas adsorption quantity is reduced [19]. Compared between the kinetic promoters of K_2CO_3 and diethanolamine (DEA), the maximum gas adsorption of CO_2 by using dry-K_2CO_3-water is slightly lower, but the kinetics is faster than dry-DEA-water [20]. Recently, a dry-K_2CO_3-containing-water prepared by surface modified interface-active mesoporous silica particles can enhance the CO_2 capture in both adsorption rate and capacity [21].

Cyclodextrins (CDs), as an additive agent, have already been applied in various fields, including foods, agriculture, pharmaceuticals, cosmetics, and so on [22–26]. CDs are crystalline, homogeneous, and non-hygroscopic substances, which are torus-like macro rings built up from glucopyranose units. The α-CD comprises six glucopyranose units, and β-CD comprises seven such units. The ring that constitutes the CDs, in reality, is a cylinder, or better said a conical cylinder, which is frequently characterized as a doughnut or wreath-shaped truncated cone. The cavity is lined by the hydrogen atoms and the glycosidic oxygen bridges. The nonbonding electron pairs of the glycosidic oxygen bridges are directed toward the inside of the cavity producing a high electron density there and lending to it some Lewis base characteristics. Because of the external hydrophilic and internal hydrophobic properties, the application of CD is mainly intended for the entrapment of small molecules, and stabilization of reactive intermediates [27]. In 1950s, the feasibility of gas encapsulation by α-CD cavity was firstly investigated [28]. Then, aqueous α-CD was reported to include gas hydrocarbons (CH_4, C_2H_6, C_3H_6), and some small inorganic molecules like Cl_2, Kr, O_2 and CO_2 to form clathrates [29,30]. The high affinity of CO_2 for complex formation is utilized for the isolation of α-CD through the precipitation of a gas inclusion complex [31]. Gas purification based on the selective adsorption of gas mixture onto an adsorbent material was then discussed by Atwood et al [32].

Considering the advantages of CD in gas capture, we prepared several DWs by using CD solutions to intensify the gas adsorption process. The DWs prepared with CD solutions are called dry-cyclodextrin-water, which are marked as DCD. According the different CDs we used (α-CD and β-CD), the DCDs were also labeled as α-DCD and β-DCD, respectively. We found that the added α-CD can improve the adsorption for both CH_4 and CO_2 gases, while the adsorption of CO_2, however, is inhibited in β-DCD. The total gas adsorption amount and its rate are related to the gas diffusion, hydrate formation, CD inclusion formation, and the change of pore size of DCD. In this paper, systematic experimental studies were performed, and a mathematical model was proposed to describe the gas adsorption kinetics in DCD.

2. Experimental section

2.1. Materials and synthesis

Pure carbon dioxide gas (99.99%) and methane gas (99.999%) were supplied by Beijing YangLilai Chemical Gas Co., Ltd. (China), while α-cyclodextrin (AR, 99.9%) and β-cyclodextrin (AR, 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Hydrophobic silica particles, SIPERNAT D10, were supplied by EVONIK (Germany). The static contact angle and mean particle size of D10 are 119° and 6.5 μm.

According to the solubility of CD in water, firstly we prepared a series of CD solutions with different concentration from 0 to its saturation. For α-CD solutions, 0 g, 3 g, 6 g, 9 g and 12 g α-CD were added to 100 g pure water, respectively. And for β-CD solutions, the qualities of cyclodextrin added to 100 g water were 0 g, 0.4 g, 0.8 g, 1.2 g and 1.6 g, respectively. The concentration of CD solution will be expressed in g (cyclodextrin)/100 g (pure water) in this paper. After the preparation of different CD solutions, the α-DCD and β-DCD were then synthesized. All of DCDs were prepared by mixing 5 g of hydrophobic silica and 95 g CD solutions with different concentrations, and stirred with ~19,000 rpm for 90 s in a domestic blender.

2.2. Kinetics measurement

Various DCDs with same mass of 22.0 g were loaded into a 300 mL miniature high pressure reactor (SLM-200, China), respectively. A circulator bath (DTY-10B, China) was connected to the reactor for temperature controlling to a certain value from 291 K to 271 K. The reactor was then pressurized with CO_2 or CH_4 gases as required and sealed. Gas adsorption kinetics in DCD can be studied by observing the gas pressure change as a function of time under different temperatures, and then an optimal temperature for gas adsorption was obtained. For CH_4, the experimental temperature and initial pressure were 277 K and 8.5 MPa, while 277 K and 3.5 MPa for CO_2. There is no mechanical agitation employed during each gas adsorption process.

3. Results and discussion

3.1. Optimal temperature of gas adsorption capacity

For insoluble small gases, such as CO_2 and CH_4, gas hydrates were considered as the final products of guest gas stabilized in DW, and higher pressure can improve the nucleation of gas hydrates. In this work, the initial pressures of CO_2 and CH_4 were controlled at 3.5 MPa and 8.5 MPa, respectively, which satisfied the requirement of insoluble gas adsorption in DW. Temperature is a key factor to affect gas adsorption kinetics, and it is necessary to find a suitable temperature that DW has a maximum gas adsorption capacity. For CH_4 and CO_2, the amount of adsorption is lower at room temperature, and the gas is dissolved in water. However, the amount of adsorption has increased in the low temperature, and the gas hydrate structure began to form in the conditions of low temperature and high pressure. The effect of temperature on CH_4 adsorption kinetics has been reported [11], and the temperature range from 0.0 °C to 4.0 °C was considered to be optimal. While for CO_2, the temperature effect on adsorption kinetics in DW is investigated, and the results are shown in Fig. 1. One can see that when temperature is higher than 7.0 °C, the DW has nearly no capacity to adsorption gases. With temperature decreasing from 7.0 °C to 4.0 °C, the CO_2 adsorption capacity (defined as the scaled volume of guest gas adsorbed at standard pressure per unit volume of DW, V/V) increases to maximum gradually.

If the temperature decreases to −2 °C continuously, the capacity will be decreases dramatically but the initial adsorption rate increases.