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Synergic effect of cyclopentane and tetra-n-butyl ammonium bromide on hydrate-based carbon dioxide separation from fuel gas mixture by measurements of gas uptake and X-ray diffraction patterns

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ARTICLE INFO

Article history:

Received 28 June 2011

Received in revised form

14 September 2011

Accepted 16 September 2011

Available online 11 October 2011

Keywords:

TBAB

CP

IGCC

Gas uptake

Hydrate

CO₂ separation

ABSTRACT

The synergic effect of Cyclopentane (CP) and Tetra-n-butyl Ammonium Bromide (TBAB) on the hydrate-based carbon dioxide (CO₂) separation from IGCC (Integrated Gasification Combined Cycle) syngas is investigated by measuring the gas uptake and the power X-ray diffraction (PXRD) patterns in this work. The CP with CP/TBAB solution ratio of 5 vol% added into the 0.29 mol% TBAB solution can remarkably increase the gas uptake at 4.0 MPa and 274.65 K. The PXRD patterns of the semi-clathrate (sc) hydrate and structure II (sII) hydrate are obtained for the CP/TBAB/gas/H₂O system. The synergic effect of the CP and the TBAB includes two aspects: On one hand, the CP molecules housed in the hollow centers of the large cavities together with TBAB cations (TBA⁺) make the sc hydrate more stable. On the other hand, the TBA⁺ displaced out of the large cavities by the CP molecules make the ionization reaction of TBAB in the solution going toward the reverse direction. Thus, the more TBAB molecules exist in the solution and form the more sc hydrate, resulting in the considerable increase of the gas uptake.

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1. Introduction

Carbon dioxide (CO₂) is considered as the main contributor to the greenhouse gases resulting in global warming, and about one third of all CO₂ emissions worldwide are produced by fuel power plants [1,2]. Hence, the CO₂ capture from fossil power plants is a prime target to slow down the deterioration of the climate. Recently, the integrated gasification combined cycle (IGCC) is widely utilized in coal-fired power plants. Thus

separating CO₂ and purifying H₂ from IGCC syngas becomes one important project for the industrial application. The conventional techniques for the CO₂ separation include physical adsorption, chemical adsorption, cryogenic fractionation and membrane process. However, the above techniques have their individual issues of either high cost, large energy consumption, low capacity or high corrosion respectively [3]. Therefore, for the purpose of utilizing fossil fuels in the power plants continuously, it is necessary to develop the

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new technologies to capture CO₂ and purify H₂ efficiently and cost-effectively. Such a technology is a hydrate-based technology of the gas separation and its mechanism is on the selective partition of the components in the hydrate phase and in the gas phase [1]. Because the equilibrium hydrate formation pressure of CO₂ is much lower than that of H₂ at the same temperature, it is expected that CO₂ preferentially encaged into the hydrate crystal phase. The hydrates crystals are separated and subsequently decomposed to create the CO₂-rich stream, while the rest constitute the CO₂-lean one.

Gas hydrates are non-stoichiometric crystalline compounds composed of “host” lattices and “guests” molecules. The “host” lattices are made up of hydrogen-bonded water molecules, the “guests” are those molecules in suitable sizes and shapes [4]. The compounds are generally in four distinct structures including structure I (sI), structure II (sII), structure H (sH) and semi-clathrate (sc) according to the differences of sizes, shapes and cages. At moderate pressures in the range of a few MPa, CO₂ forms hydrates sI [5], whereas H₂ forms hydrates sII at high pressure of 200 MPa or at low temperature of 80 K [6]. Sugahara et al. reported that H₂ does not occupy any cages of hydrate sI based on Raman spectroscopy study on a single CO₂/H₂ hydrate crystal [7]. The pure CO₂ is known to occupy both 5¹² and 5¹²6² cages of sI hydrate with a unit cell parameter of 11.893 Å [8]. Furthermore, in the similar condition, the structure of CO₂/H₂ mixture hydrate is identified to be the sI hydrate [9,10].

In order to meet the requirement of CO₂ capture from fuel gas mixture in the industrial application, the main challenges for the hydrate-based CO₂ separation and capture from fuel gas mixture are reducing the hydrate induction time, improving the gas uptake and enhancing the separation efficiency. Therefore, different additives or promoters are employed to moderate the condition of the hydrate-based CO₂ separation from IGCC syngas, raise the hydrate formation rate, and improve the CO₂ separation efficiency. Tetrahydrofuran (THF) was found to be effective on reducing the CO₂/H₂/H₂O hydrate formation equilibrium pressure, and the concentration of 1.0 mol% was identified to be the optimum concentration in the experiments of the hydrate-based CO₂ capture [11]. Based on the find that the hydrate formation equilibrium pressure of H₂/CP ternary hydrate is lower than that of H₂/THF ternary hydrate at the same condition, CP was used in the process of hydrate-based CO₂ capture from CO₂/H₂ gas mixture by Zhang and Lee [12]. Both CP hydrate and THF hydrate were identified as sII hydrates [13]. TBAB is also widely employed as a hydrate promoter to capture and separate CO₂ from fuel gases [14–18]. Li et al. found that 0.29 mol% TBAB is the optimum concentration to obtain the highest CO₂ separation efficiency [16,19]. According to the studies made by Strobel et al. [20] and Shimada et al. [21], a typical structure of the hydrate involving in TBAB is semi-clathrate (sc) with six small dodecahedral cavities (5¹²) and four large cavities composed of two tetrakaidecahedra (5¹²6²) and two pentakaidecahedra (5¹²6³). CO₂ and H₂ molecules can be enclosed in the cavities selectively. According to the results of the studies [19,22], the CO₂ separation efficiency for CP/gas hydrate is small and the induction time for forming TBAB/gas hydrate does still not meet the requirement of instantaneously forming hydrate in the industrial application. Therefore, Li et al. [23] used TBAB solution in conjunction with CP as a mixed promoter to

separate CO₂ from IGCC syngas. The results showed that the synergistic effect of CP and TBAB is helpful to increase the gas uptake and separation efficiency. Nevertheless, the mechanism of the synergistic effect is not quite clear and needs to be further identified. Power X-ray diffraction (PXRD) is the well-known tool used for solid phase structural analysis at a molecular level, and it is also used for gas hydrate analysis to obtain information on crystal structure, crystal dimension/volume, and composition/cage occupancy values [24].

Based on our previous work [23], the 0.29 mol% TBAB solution in conjunction with CP is employed in this work, and the volume ratio of CP/TBAB solution in the system is 5.0 vol%. The gas uptake and the induction time are obtained in the process of the hydrate-based CO₂ separation from the CO₂/H₂ mixture at 4.0 MPa and 274.65 K. Subsequently, the synthetic hydrate samples obtained from the different systems, such as CP/gas/H₂O, TBAB/gas/H₂O, CP/TBAB/gas/H₂O, at 153.15 K and atmosphere pressure are analyzed by the power X-ray diffraction (PXRD) to confirm whether the hydrates of CP/gas, TBAB/gas, the hydrate containing CP, TBAB and mixture gas exist and to verify the structures of the hydrates. Furthermore, the synergistic effect of CP and TBAB resulting in the more gas uptake and the higher separation efficiency is identified by the analysis of the PXRD patterns.

2. Experimental

2.1. Materials

The gas mixture of CO₂/H₂ (61.4/38.6%) simulating the IGCC syngas is supplied by Foshan Huate Gas Co., Ltd. TBAB with a purity of 99.9% and CP with a purity of 99.0% are supplied by Chengdu Best Reagent Co., Ltd. The de-ionized water with the resistivity of 18.25 mΩ cm⁻¹ is produced with an ultra-pure water machine which is supplied by Nanjing Ultrapure Water Technology Co., Ltd.

2.2. Gas uptake and separation efficiency measurement

Fig. 1 shows the schematic of the experimental apparatus. As shown in Fig. 1, the crystallizer (CR) with inner volume of 336 ml and a supply vessel (SV) of 1350 ml are made of 316 stainless steel. They are immersed in a water bath in which the temperature is controlled by a proportional integral derivative (PID). There are two circular viewing windows made of Plexiglas on the front and back of the CR. A pump is connected on the CR to inject the solution into the CR and pump the gas out from the CR. The maximum working pressures of the CR and the SV are 25 MPa, respectively. The pressures in the CR and SV are measured with two Setra smarte pressure transducers (model 552, Boxborough, MA, USA) with the uncertainty of 0.02 MPa, respectively. The temperature in the water bath and the temperature of the gas phase and the liquid phase in the CR are measured by using three Pt1000 thermocouples (JM6081) with uncertainties of 0.1 K, respectively. Under the CR, a magnetic stirrer (0–1000 r/min) is employed to mix the contents in the CR thoroughly. The compositions of the residual gas phase and the decomposition gas phase are determined with a HP6890 gas

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