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Hydrate-based hydrogen purification from simulated syngas with synergic additives

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ABSTRACT

Hydrated-based separation process has recently raised as a novel technology for hydrogen (H_2) purification from mixture gases containing carbon dioxide (CO_2). However, the practical application requires suitable hydrate formation condition, hydrate formation rate, gas selectivity, gas storage capacity and so on. This work presents the effect of synergic additives on the hydrate-based syngas purification process based on the thermodynamic, kinetic, purification characteristic studies as well as microcosmic structure analysis. The synergic additives comprise traditional hydrate promoter (tetra-n-butyl ammonium bromide, TBAB) and gas solvent (dimethyl sulfoxide, DMSO). 40.2 mol% CO_2/H_2 binary mixtures were selected as the simulated syngas. The results show that the synergic additives (TBAB-DMSO) can reduce the equilibrium hydrate formation pressure of the simulated syngas by 80%. Compared to single TBAB for the hydrate-based purification process, the synergic additives could improve the gas consumption rate of the unit system, gas storage capability and gas selectivity by about 32%, 105% and 51% respectively, and decrease the loss ratio of H_2 by 1.45%. The Raman analysis reveals that the simulated syngas forms semiclathrate framework with TBAB-DMSO. DMSO only performs as a gas solvent during the gas dissolution and diffusion process, and not participates in the hydrate framework formation.

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Introduction

Recently, the interactional affect between climate and humankind has become even more violent [1]. Human influence on the climate system is unequivocal, and alternately it is widespread impacted by the climate changes (especial global warming). It is widely accepted that the global warming is mainly attributed to the greenhouse gas (GHG) (mainly carbon dioxide (CO_2)) emissions related to fossil fuels energy [2]. According to the fifth assessment synthesis report of Intergovernmental Panel on Climate Change (IPCC), CO_2 emissions related to fossil fuels (like oil, coal and natural gas) had reached about 32 $GtCO_2$ in 2010, which contributed about 78% to the total GHG emission [3]. Continued GHG emission will cause further warming and increase the likelihood of severe, pervasive, and irreversible impacts for people and ecosystems. Globally, however, economic and population growth continue to be the most important drivers of increase in CO_2 emissions from fossil fuels, which will continue to represent the worldwide primary energy in the near future [4]. According to International Energy Agency, for instance, as the second source of primary energy after oil worldwide, coal account for approximately 40% source for the world's electricity generation [5], and its utilization in the worldwide will still increase in the coming decades. Therefore, substantial and sustained reductions in GHG emissions from worldwide energy consumption are required. Decarburizing energy generation (like pre-combustion CO_2 capture and storage) is a key cost-effective mitigation strategy to limit global warming to below 2 °C relative to pre-industrial levels [3]. The principle of this process is that, before the combustion process, fossil fuels are gasified (like coal and biomass) or steam reformed (like natural gas and liquid hydrocarbons) to produce synthesis gas (syngas) [6]. Syngas derived from gasification or steam reforming can be shift into gas mixture, which only contains hydrogen (H_2) and CO_2. In this case, carbon component in fossil fuels can be separated and captured before combustion or utilization, while the resulting H_2-rich syngas can be subsequently utilized as power plants or vehicles fuel with essentially zero emissions. It is worthy to note that hydrogen energy has been proposed as an ideal long-term solution to energy-related environmental and supply security problems [7]. Thus, purification of hydrogen from syngas is significant for both energy and environment problems. In order to achieve this goal, a wide variety of the separation techniques such as pressure swing adsorption (PSA), amine scrubbing, and membrane reactors are being pursued, although some have been proven to have critical problems associated with large energy consumption, corrosion, foaminess, and low capacity and others [8,9].

Hydrate-based CO_2 capture and hydrogen purification process, as a promising and novel method, has attracted widely attention due to the excellent characters such as high gas storage potential [10], environmentally friendly [11], and low energy penalty and low cost [12,13]. Hydrates are non-stoichiometric crystalline inclusion compounds, which are formed by different types of guest molecules enclathrated in the hydrogen bond network of water molecules at moderate conditions (low temperature and high pressure) [14]. Moreover, the thermodynamic conditions for hydrate formation with different guests are mainly dependent on the difference of the guest molecules (such as size and shape) [15]. Hydrate-based hydrogen purification technology is based on the selective partitioning of the components in the hydrate phase and in the gas phase [9,16]. For the syngas, the CO_2 component has relatively moderate hydrate formation condition, which is helpful to preferentially form CO_2 hydrate with high thermodynamic stability [10], resulting in a CO_2-rich in hydrate phase and leaving H_2-rich in the residual gas phase [17]. Hence, the high selectivity can be expected for the hydrate-based H_2 purification from the mixtures accompanied with CO_2.

A commercially viable hydrate-based hydrogen purification process requires moderate operation condition, rapid hydrate formation rate, high gas selectivity, and satisfactory gas storage capability. For the moderate operation, some thermodynamic promoters such as cyclopentane (CP) [18–21], tetrahydrofuran (THF) [22–25], propane (C_3H_8) [26–30], tetra-alkylammonium/alkylphosphonium salts tetra-n-butyl ammonium bromide (TBAB) [31–40] etc. were successfully developed to reduce the hydrate formation pressure. However, the other three essentials (hydrate formation rate, gas selectivity, and gas storage capability) have yet still hindered the further development and application of hydrate-based hydrogen purification technology. To break the bottleneck, the current solutions mainly focus on kinetic promoters, porous medium, and gas/liquid contact technologies. For instance, sodium dodecyl sulphate (SDS) is used to increase the hydrate formation rate and gas capacity [41–43]. Additionally, some straightforward way such as mixing, spray and bubbling are used to promote the dissolution of gas molecules and improve the gas/liquid contact [44,45], but which is at the cost of power consumption. Recently, the porous media of silica gels have attracted many attention, which have been reported could enhance the hydrate formation rate and the gas-water conversion ratio [27,46–51]. However, it is noted that the added sands or gels also occupied the system volume, and the hydrate formation rate and gas storage capability for unit system was still lower.

Rather than the above approaches, the previous researchers have proved that a higher solubility of hydrate forming gas molecules in water and a larger contact area between the hydrate formers and water can reduce the mass transfer resistance and result in a faster hydrate formation rate [52,53]. In fact, only enough gas molecule dissolution and diffusion in the water probably cause the hydrate nuclear and growth rapidly [15]. Consequently, it is possible to reduce the interstitial water, enhance the hydrate growth rate, and improve gas selectivity and gas storage capability by improving the gas dissolution and diffusion processes, using the physical gas solvents in conjunction with the traditional hydrate promoters. Recently, we have investigated the thermodynamic properties of the landfill gas hydrate formation with the synergic additives based on the gas solvent [54], and found that the synergic additive based on the gas solvent have a considerable promotion effect on the CO_2 dissolution process and the subsequent hydrate formation process. Thus, it would be interesting to insight whether the synergic additive is equally significant for the hydrate-based syngas purification