



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Deep regeneration of activated carbon catalyst and autothermal analysis for chemical looping methane thermo-catalytic decomposition process

Li Yang, Fang Liu^{*}, Yang Liu, Wenbin Quan, Jianlong He

School of Electrical and Power Engineering, China University of Mining and Technology, Xuzhou, Jiangsu Province, 221116, China

ARTICLE INFO

Article history:

Received 5 February 2018

Received in revised form

13 June 2018

Accepted 30 July 2018

Available online 23 August 2018

Keywords:

Chemical looping methane decomposition

Activated carbon

Catalytic activity

Heat balance

ABSTRACT

The application of a chemical looping process to methane thermo-catalytic decomposition using activated carbon (AC) as a catalyst has been recognized as a promising technology for continuous high-purity H₂ production in a carbon constrained world. However, it usually needs an external heat supply for the endothermic decomposition reactions. By taking advantage of the chemical looping combustion (CLC) technology, this study proposed a deep regeneration approach using H₂O and O₂ as regeneration agents to overcome the issues with maintaining catalytic activity and producing the heat needed for the endothermic reactions of H₂ production from methane. TG-DTA and bench scale fluidized bed experimental results indicate that a deep regeneration degree of 30% or above could completely reactivate the spent AC catalyst and simultaneously generate sufficient heat than required in the methane decomposition reaction. Characterization study implies that the deep regenerated AC catalyst could maintain its physical properties within a certain number of cycles. Based on the experimental results, the chemical looping methane thermo-catalytic decomposition process was further optimized and assessed by Aspen Plus[®] thermodynamic simulation. The results indicate that heat and mass balances could be attained, and the circulation of the AC catalyst with a temperature difference of 262 °C between the decomposer and the regenerator enabling the process to run autothermally.

© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

The demand for hydrogen (H₂) has increased by more than 50% in the past 10 years, and is still rapidly increasing worldwide [1]. Currently, the state of the art process used for H₂ production is steam methane reforming [2].

However, the H₂ produced by this multiple-step method is unavoidably accompanied by a large amount of CO₂ emission both from the process itself and the input energy for the process. Hence, if H₂ combustion/utilization is to become the ultimate approach for producing clean energy, an urgent need exists to develop CO₂-free H₂ production technologies [3,4].

^{*} Corresponding author.

E-mail address: fang.liu@cumt.edu.cn (F. Liu).

<https://doi.org/10.1016/j.ijhydene.2018.07.202>

0360-3199/© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Natural gas production continues to grow, and has significantly displaced the use of coal for power generation. Although the use of natural gas for power generation produces significantly less CO₂ per unit energy than does coal, the CO₂ concentration in the flue gas is low which results in a more complicated CO₂ capture process for clean energy production scenarios [5]. Thereby, considering the increasing demand for H₂ or natural gas decarbonization to meet environmental emission requirements, the direct decomposition of methane for H₂ production has attracted renewed interest. This direct decomposition is expressed as:



Thermodynamic analysis shows that it is possible to produce pure H₂ with 100% methane conversion at temperatures of 1000 °C and above [6]. Thus, the primary benefit of CH₄ decomposition, if operated higher than 1000 °C and with an external energy supply, is that the products are only solid carbon and gaseous H₂. Solid carbon can be sequestered, leading to an outlet stream of pure H₂. Another advantage in direct decomposition of methane is its smaller energy consumption per mole of H₂ produced, 37.4 kJ/mol, as compared to 63.3 kJ/mol H₂ for steam reforming of methane [7]. Although direct decomposition requires a much higher temperature (>1200 °C) than reforming to achieve a reasonable yields [8], it is possible to use catalysts to lower the reaction barrier. Transition metals such as Ni, Fe, and Co-based catalysts have been widely investigated [6,8,9]; Ni-based catalysts have been shown to be highly effective with fast reaction rates. However, these metal-based catalysts suffer from high cost and rapid deactivation caused by carbon deposition [10–12]. Carbon deposits and the concomitant catalyst deactivation are a result of encapsulating carbon that covers the surface active sites and carbon deposition underneath the active metal particles that pushes the metal particles away from the support [13–15]; carbon deposited between the metal particles and the support is very difficult to remove without destroying the catalyst structure and catalyst activity. Great effort has been undertaken to regenerate those metal-based catalysts. However, Moliner et al. [16] pointed out that neither regeneration nor separation of metal-based catalysts from deposited carbon is feasible. Another consideration for using metal-based catalysts is their relatively low operating temperatures. Ni-based catalysts, for instance, are reported to have a maximum operating temperature of 600 °C, the low temperature causes thermodynamic limitations on methane conversion [17]. Overall, considerable constraints exist that impede the application of metal-based catalysts for commercial, high purity H₂ production.

Recently, cost-effective carbonaceous-type catalysts were found to have a reasonable catalytic activity in methane decomposition [18,19]; they also could be used at higher temperatures than transition metal based catalysts [20]. Among these carbonaceous catalysts, carbon materials in a disordered form usually yields a better catalytic performance than ordered ones. For the disordered form of carbon material, activated carbon (AC) typically has large surface areas, and is found to provide the highest initial methane decomposition rate [20,21]. The kinetics study indicated that the application

of AC catalyst could greatly decrease the methane decomposition activation energy, reducing it to a level of less than 200 kJ/mol [19,22]. The catalytic role of activated carbon material was attributed to its large surface area, surface oxygen functional groups and the structural defects, which serves as active sites for decomposition reaction [23–26]. Liu performed a detailed characterization study, and found that comparing with the surface oxygen functional groups, the BET surface area played a more important role in maintaining its catalytic activity [27]. Furthermore, AC catalysts have a medium density and adjustable particle sizes that make them highly suitable for use in fluidized bed reactors. However, similar to metal-based catalysts, activated carbon also suffered from rapid deactivation as was expected when carbon deposition occurs in catalytic reactions [22,28–30]. Fortunately, carbon deposition on AC catalysts only occurs on the surface and may be more easily removed, enabling AC catalysts to be reactivated more easily than transition metal catalysts [27].

CO₂, air and steam are typically used to regenerate spent AC catalyst, for instance, Pinilla et al. [31] conducted 3 decomposition and regeneration cycles, and Abbas et al. [32] performed 5 cycles using CO₂ as a regeneration agent; they both reported a significant decrease in initial activity after each regeneration cycle. The decreased activity was attributed to a high resistance of the deposited carbon to CO₂ gasification [31]. It has also been shown that O₂ or steam by themselves cannot completely reactivate spent AC catalysts [8] although the extent to which regeneration occurred by using steam was much faster [33]. Traditional regeneration process usually keeps the mass of the original catalyst unchanged, however, the regeneration degree is adjustable, to better resume the catalytic activity, the regeneration degree could go a little further, making it a deep regeneration. Our previous study [27] showed that steam can completely regenerate spent AC catalyst if deep regeneration is used in which some decrease of the catalyst mass occurred. A continuous high-purity H₂ production process, diagram as shown in Fig. 1, by applying a chemical looping technology to methane thermo-catalytic decomposition using AC as the circulating material was proposed [27], in which two interconnected reactors, a decomposer and a regenerator, are used. In the decomposer, with the aid of AC catalyst, methane is decomposed to solid carbon and H₂, thus a nearly pure H₂ stream can be obtained at appropriate conditions. And in the regenerator, the spent AC catalyst is reactivated by a controlled steam gasification process to remove the deposited carbon, and syngas is produced simultaneously.

The reactions in both reactors in Fig. 1 are endothermic, thereby requiring the supply of additional, external heat. However, it may be more efficient if the process was self-regulated to have heat balance similar to that in an autothermal process. Autothermal processing is regularly practiced in chemical looping combustion (CLC) technology [34–38]. Relative to H₂ production from methane in Fig. 1, heat could be generated during spent catalyst regeneration, so in the regenerator, not only the catalytic activity resumption, but the amount of heat produced from the regeneration should also be considered. Similar as the role of oxygen carriers (OCs) applied in CLC [39], AC catalyst adsorbs heat in the regeneration reaction, and that heat contained within the hot

Download English Version:

<https://daneshyari.com/en/article/8954932>

Download Persian Version:

<https://daneshyari.com/article/8954932>

[Daneshyari.com](https://daneshyari.com)