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Application of chemical looping process for continuous high purity hydrogen production by methane thermocatalytic decomposition

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ARTICLE INFO

Article history:

Received 3 November 2015

Received in revised form

1 January 2016

Accepted 7 January 2016

Available online 3 February 2016

Keywords:

Chemical looping process

Methane thermocatalytic decomposition

Hydrogen production

Activated carbon catalyst

Durability

ABSTRACT

Methane thermocatalytic decomposition has been recognized as an advanced process for hydrogen (H₂) production or natural gas decarbonization in the carbon constrained world due to its low CO₂ emission. As an alternative to costly transition metal catalysts, it is believed that carbon materials are promising catalysts for this process, of which activated carbon (AC) provides reasonable reaction kinetics.

The application of a chemical looping process to methane thermocatalytic decomposition is investigated for continuous high purity H₂ production using AC as a catalyst. To be suitable for a fluidized bed-based chemical looping process, the AC catalyst should meet certain requirements besides its contribution to reaction kinetics. Accordingly, it was evaluated by durability, crushing strength, and resistance to agglomeration. The evolution of textural properties and surface chemistry is examined as well to understand the catalytic activity performance. The results show that, under proper regeneration, the AC catalyst demonstrates no deactivation during cyclic study and prove that high purity CO₂-free H₂ can be continuously produced. The crushing strength of AC catalyst is suitable for a chemical looping process and no agglomeration is observed under parameters tested. In addition, the experimental data also indicated that surface area plays an important role in the cyclic catalytic activity of the AC catalyst.

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Introduction

The atmospheric CO₂ concentration continues to increase in recent years and has exceeded 400 ppm [1]. Human activity is widely accepted as responsible for distorting the balance of

the carbon cycle [2]. Coupled with the increasing global energy demand and the increasing concerns about climate change due to CO₂ release from the combustion of fossil fuels, there is now an urgent need to develop clean and renewable energy systems for hydrogen production [3]. Currently, the main process used for hydrogen (H₂) production is steam methane

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<http://dx.doi.org/10.1016/j.ijhydene.2016.01.023>

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reforming [4,5]. However, the H₂ produced by this multiple-step method is unavoidably accompanied by a large CO₂ emission both from the process itself and the energy needed for the process.

With the increasing demand for hydrogen and natural gas decarbonization to meet environmental requirement, direct methane decomposition for the purpose of hydrogen production has attracted renewed interest, as expressed as:



The thermodynamic analysis shows that it is possible to produce pure H₂ with 100% methane conversion at temperatures above 1000 °C [6]. Thus the primary benefit of CH₄ decomposition, if operated higher than 1000 °C and with external energy supply, is that the products are only solid carbon and gaseous H₂, of which solid carbon can be sequestered, leading to an outlet stream of pure H₂. Another advantage is the theoretical less energy consumption per mole of H₂ produced, 37.4 kJ/mol H₂ for methane decomposition compared to 63.3 kJ/mol H₂ for steam methane reforming [7].

Direct methane decomposition requires a high temperature to obtain a reasonable yield [8]. The use of a suitable catalyst can dramatically decrease the temperature requirement. Transition metal-based catalysts, such as Ni, Fe, and Co-based catalysts, have been widely investigated for this application [6,8–10]. The Ni and Co-based catalysts are considered to be the most effective catalysts resulting in the fastest methane decomposition rate [10]. However, challenges for these metal-based catalysts include high cost, low mechanical strength and rapid catalyst deactivation [6,11–13]. The deactivation mechanism is described as the deposit of produced carbon on the catalyst and the subsequent formation of encapsulating carbon, thus the active metal particles become encapsulated [6]. Besides surface deposition, the produced carbon also grows under the active metal particles, and will push the metal particles away from the support [6,8,14–16], which makes it very difficult to be removed or combusted without destroying the catalyst structure. Great effort has been undertaken to regenerate metal catalysts. However, Moliner et al. [17] pointed out that neither regeneration nor separation of metal-based catalysts from deposited carbon is feasible. Another limitation of those metal-based catalysts is their relatively low suitable operating temperatures [18], which in turn thermodynamically limited the methane conversion. These constraints impede the application of metal-based catalyst for large scale high purity H₂ production.

A cost-effective regenerable catalyst is urgently needed for practical methane decomposition in industrial applications. Muradov [19,20] found that elemental carbon had a catalytic function in methane decomposition and was available at a lower cost than metal-based catalysts. Additionally, carbon catalysts exhibit high temperature resistance [20,21]. Among the available carbon catalysts, activated carbon (AC) and carbon black (CB) are the most often proposed catalysts for catalytic CH₄ decomposition [20,21], and some other low cost carbon catalysts such as coal char and coal liquefaction residue have also been investigated [22,23]. Generally, CB demonstrates lower catalytic activity in methane decomposition,

but its deactivation is slower [24–27], while AC provides a higher initial methane decomposition rate but its catalytic activity deactivates more rapidly [28–32]. The deactivation is attributed to the monophonic carbon deposition on the AC surface [29,31]. Compared to metal-based catalysts, the carbon deposition mechanism on AC is different. The deposited carbon grows on the AC surface, and may be removed, enabling the AC catalyst the ability to resume its catalytic activity. Thus, AC could be a promising catalyst for continuous, high purity H₂ production if an effective method for removal of the deposited carbon is developed.

Regeneration of the spent AC was first proposed by Muradov [20,33]. Several regenerating agents such as air, CO₂ and steam were tested, and steam or steam with CO₂ regenerated AC were reported to exhibit a better catalytic activity than the spent AC. Pinilla et al. [34] conducted 3 decomposition and regeneration cycles and Abbas et al. [35] did 5 cycles using CO₂ as a regeneration agent; they both reported a significant decrease in initial activity after each regeneration step. The reason was explained that the deposited carbon presented more resistance to CO₂ gasification than the catalyst did [34]. Compared to CO₂ regeneration, steam regeneration is much faster [36], and may have the potential to remove the deposited carbon completely. Spent catalyst regeneration is still a major challenge for methane decomposition [37]. There is limited information in open literature discussing deposited carbon removal by steam carbon gasification, and the performance and evolution of steam regenerated activated carbon under successive decomposition and regeneration cycles is still not well studied.

The interest of this paper is continuous production of high purity hydrogen. With a regenerable AC as a catalyst, continuous high purity hydrogen production can be realized by applying a chemical looping process to methane thermocatalytic decomposition. The process concept diagram is proposed in Fig. 1, in which two interconnected reactors, a decomposer and a regenerator are applied. In the decomposer, with the aid of the AC catalyst, methane is continuously converted to solid carbon and hydrogen, and a nearly pure hydrogen stream can be obtained at the outlet under appropriate conditions. The decomposer can be designed as a bubbling fluidized bed or a moving bed to enhance the methane gas residence time to reach reaction equilibrium. Carbon particles exiting the reactor with the H₂ stream can be separated and collected via a solid–gas separator. The rest of the spent AC catalyst is then transferred to the regenerator where it will be regenerated via a controlled steam gasification process to remove the deposited carbon from the AC surface along with partial combustion for heat supply. The regenerator can be a bubbling bed, together with a riser to transport the regenerated AC catalyst to the decomposer via a cyclone and a loop seal. The exhaust gas from the regenerator is syngas with approximately 20–25% CO₂. The regenerated AC will be subsequently recycled back to the decomposer for a new cycle. The key features of the new process are: (1) use of a low cost AC catalyst instead of a noble metal-based catalyst for methane thermocatalytic decomposition; (2) the capability of continuous production of high purity hydrogen (~100 vol. %); and (3) the AC catalyst is regenerable.

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