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Chemical looping hydrogen production using activated carbon and carbon black as multi-function carriers

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ABSTRACT

The application of a chemical looping process for methane thermo-catalytic decomposition using activated carbon (AC) as a catalyst has been recognized as an advanced process for continuous high-purity H₂ production in the carbon constrained world due to its low CO₂ formation. AC is able to provide reasonable kinetics, however, it suffers from fast deactivation. Deep regeneration of spent AC catalyst using steam is able to eliminate catalytic deactivation, and this process sacrifices part of the catalyst. The catalytic performance of AC and carbon black (CB) catalysts exhibit opposite deactivation behavior with time. AC provides a better activity, but it deactivates quickly. Though the catalytic activity of CB is low, its activity not only can be maintained, but also shows an increase during the test. Our approach for AC modification was inspired by analyzing the factors that lead to the different performance. Results indicate that the catalytic performance of AC and CB exhibit opposite deactivation behavior with time, and the deposited carbon on their surfaces are in different shape, orientation, and chemical structure. The outward growing cone-like graphene layers and tubular-shaped nanostructures are key factors that help maintain the catalyst's porosity and activity; and the cause of different deposit carbon may be attributed to the irregular, cross-linking graphene layers of AC and the spherical bent graphene layers of CB.

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Introduction

The huge anthropogenic emission of CO₂ is considered the main factor leading to global warming and climate change, and much effort has been devoted to develop economic carbon capture technologies [1]. Among those CO₂ capture technologies, chemical looping combustion (CLC) is believed to be one of the most effective methods [2,3]. Instead of using air, CLC technology uses an oxygen carrier, usually a transition metal oxide or a mixture of different metal oxides, to provide

oxygen, and thus has an advantage of inherent separation of CO₂ from depleted air, enriching the concentration of CO₂. In the carbon-constrained world, based on CLC technology, chemical looping coal/biomass gasification for syngas and hydrogen production has made a great progress in recent years due to its low CO₂ production [4–10]. Hydrogen is the ultimate clean energy, and the demand of hydrogen has increased by more than 50% in the past 10 years, and is still rapidly increasing worldwide; thus, there is an urgent need to develop clean, renewable and CO₂-free hydrogen production technologies [11,12].

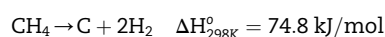
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Currently, the state of the art process used for hydrogen production is steam methane reforming [13]. However, the hydrogen produced by this multiple-step method is unavoidably accompanied by a large amount of CO₂ emission both from the process itself and the energy needed for the process. Natural gas production continues to grow, and may have the potential to significantly disrupt coal for power generation. When using natural gas for power generation or heat supply, the CO₂ concentration in the flue gas is low (<7%), resulting in a more complicated CO₂ capture 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, expressed as:



Thermodynamic analysis shows that it is possible to produce pure H₂ with 100% methane conversion at temperatures above 1000 °C [14]. 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, of which solid carbon can be sequestered, leading to an outlet stream of pure H₂. Another advantage is the theoretically smaller 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 [15].

Because of the tight C–H bonds in the methane molecule, direct methane decomposition requires a much higher temperature (>1200 °C) to achieve a reasonable yield [16]. However, a proper catalyst can dramatically decrease the temperature requirement. Transition metals such as Ni, Fe, and Co-based catalysts have been widely investigated [14,16,17], and the Ni-based catalysts are considered the most effective, resulting in the fastest reaction rate. However, challenges for these metal-based catalysts include high cost, low mechanical strength and rapid deactivation [18–20]. Deactivation is typically caused by carbon deposition, which includes two different patterns: encapsulating carbon that covers the surface active site, and carbon deposition underneath the active metal particles, which pushes the metal particles away from the support [21–23], and is very difficult to be removed or combusted without destroying the catalyst structure. Great effort has been undertaken to regenerate those metal-based catalysts. However, Moliner et al. [24] pointed out that neither regeneration nor separation of metal-based catalysts from deposited carbon is feasible. Another limitation of metal-based catalysts is their relatively low suitable operating temperatures. Ni-based catalysts, for instance, are reported to have a maximum operating temperature of 600 °C, which in turn thermodynamically limits the methane conversion [25]. These constraints impede the application of metal-based catalyst for large scale or high purity H₂ production.

A cost-effective catalyst is a basic requirement for practical methane decomposition in industrial applications. Researchers found that elemental carbon had a catalytic function in methane decomposition and was available at a much lower cost than metal catalysts [26–28]. Carbonaceous catalysts also have other merits such as high temperature

resistance and high fuel flexibility [29,30]. Among the carbonaceous catalysts, activated carbon provides the highest initial methane decomposition rate; however, similar to metal-based catalysts, it also suffers from deactivation [31–36]. It is commonly agreed that any parameter that increases the reaction rate, also increases the deactivation rate of the catalysts, as carbon decomposition occurs [37]. However, compared to metal-based catalysts, the monophonic carbon deposition only grows on the AC surface and may be removed, enabling the AC catalyst to resume its catalytic activity. CO₂, air and steam are generally used as regeneration agents. Pinilla et al. [38] conducted 3 decomposition and regeneration cycles, and Abbas et al. [39] performed 5 cycles using CO₂ as a regeneration agent; they both reported a significant decrease in initial activity after each regeneration step. The explanation was that the deposited carbon presented more resistance to CO₂ gasification than the catalyst did [38]. Compared to CO₂ regeneration, steam regeneration is much faster [40] and may have the potential to completely remove the deposited carbon. Our previous study proved that the spent AC catalyst can completely recover its catalytic activity with deep regeneration using steam as the regeneration agent [41]. Deep regeneration is to remove more carbon in the regeneration process than the amount of carbon deposited during the methane decomposition step in which there is a portion of activated carbon being removed as well. In addition, we proposed a continuous high-purity hydrogen production process by applying a chemical looping process to methane thermo-catalytic decomposition using AC as the circulating material, since AC has a medium density and an adjustable particle size distribution, which is suitable for fluidized bed reactors [41]. The process concept diagram is shown in Fig. 1, in which two interconnected reactors, a decomposer and a regenerator, are used. 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 the 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. The regenerator can be a bubbling bed, together with a riser to regenerate and transport the AC catalyst from the bottom to the top. The exhaust gas from the regenerator is syngas. The regenerated AC will be subsequently recycled back to the decomposer for a new cycle. Heat can be supplied by burning a portion of produced hydrogen or by partial oxidation of the deposited carbon. Key features of the new process are: (1) use of a low cost AC catalyst instead of a noble metal-based catalyst for methane thermo-catalytic decomposition; (2) the capability of continuous production of high-purity hydrogen (~100 vol.%); and (3) the AC catalyst is regenerable.

To successfully implement the proposed process, the performance of the AC is of vital importance. Similar to the role of oxygen carriers applied in chemical looping combustion [42–48], the AC in this process acts as a solid (carbon) carrier, a

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