CO_2-free hydrogen by catalytic decomposition of methane in a fluidized bed reactor

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The continuously rising global energy demand poses challenges with regard to the development of environmentally benign technologies. The requirement to provide large amounts of energy and simultaneously reduce pollutant emissions motivates researchers to utilize new energy carriers and develop sustainable processes. Hydrogen is one of the most promising energy carriers. Currently, the most efficient and industrially applied methods for hydrogen production include steam reforming, partial oxidation and autothermal reforming of natural gas. Although these processes are mature technologies, their common drawback is the formation of large quantities of carbon monoxide (CO) and carbon dioxide (CO_2).[1]

Methane decomposition represents an alternative to the established processes since it enables an entirely emission-free production of hydrogen based on fossil fuels.[2] Pure hydrogen and elemental carbon are the only products of this reaction. A solely thermal decomposition of methane requires elevated process temperatures above 1200 °C in order to obtain reasonable hydrogen yields.[3] By using an appropriate catalyst, the operating temperature can be decreased to 500 °C.[4]

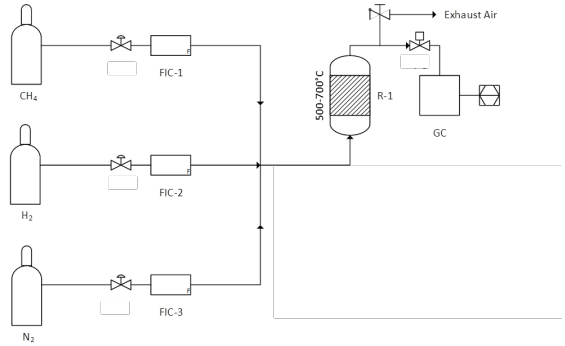
Carbon precipitates such as carbon nanofibers or nanotubes form on supported metal catalysts which are the conventional catalysts for catalytic methane decomposition (CMD). The growth process of the carbon nanostructures is induced by the metal and takes place at the metal/support interface. The metal particle is detached from the support by the formation of the nanostructure and is therefore located on the filament's tip.[5] Utilizing supported bimetallic catalysts constitutes an exception regarding the growth mechanism. SHAH *et al.*[6] observed the formation of carbon nanotubes without a metal particle on the filament's tip using binary M-Fe (M = Mo, Ni, Pd) catalysts supported on alumina. The metal particles remained anchored to the catalyst support with the carbon nanotube growing around it.

However, carbon deposition on the catalyst surface causes fast catalyst deactivation. Catalytic methane decomposition is well investigated. However, the issue of catalyst regeneration remains unsolved. Previously proposed regeneration strategies are invariably based on the combustion of deposited carbon. Combustion leads to the release of CO_2, diminishing the environmental appeal of a sustainable hydrogen economy. A suitable catalyst regeneration strategy to enable a continuous process together with valorization of the produced carbon filaments are key aspects. These factors will render catalytic methane decomposition economically competitive with conventional hydrogen production processes. Investigations of the decomposition reaction in a fluidized bed reactor realized by JANG and CHA[7] provide a good starting point. The authors observed carbon attrition from the catalyst surface. Moreover, the methane conversion rate was maintained via attrition of the deposited carbon. At the same time, AMMENDOLA *et al.*[8] developed a model for catalytic methane decomposition in a fluidized bed reactor. Their calculations indicate that carbon attrition is possible and plays a key role in the regeneration of the external catalyst surface.

Based on these findings, we combined mechanical carbon attrition with the utilization of supported bimetallic catalysts as a potential catalyst regeneration strategy for the CMD process. The intention is to perform CMD in a fluidized bed reactor. A periodic switch between fixed-bed conditions and turbulent flow of the catalytic bed induces inter-particle collisions shearing the carbon filaments from the catalyst. Due to the density difference, carbon nanostructures can be carried away by the fluidizing gas stream and subsequently collected as a valuable product. The catalyst remains in the reactor to allow a continuous operation of CMD. The obtained carbon nanostructures do not contain metal particles eliminating the need for extensive purification steps.

Based on the reviewed results a reactor system was designed that enables catalyst regeneration trough carbon attrition. The experimental setup consists of three main subsystems: (i) a reactor combined with a heating source; (ii) a gas controlling and delivery subsystem; and (iii) an analytical subsystem. Methane serves as the substrate gas whereas a hydrogen-feed line enables reduction of the catalyst *in situ*. Additionally, a nitrogen feed-line is integrated into the reaction system in order to induce turbulent flow of the catalyst bed. The setup is constructed in such way that temperatures as far as 1200 °C and a gas flow of up to 20 L/min can be realized. The composition of the product gas stream is determined by online gas chromatography (GC).

Overall the described combination of tailored catalyst design with the selection of an appropriate process setup provides the opportunity for CO_2-free hydrogen production.



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