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Editorial

Fuel Processing Technologies for Hydrogen Production from Methane

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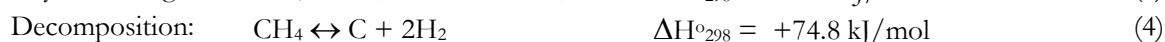
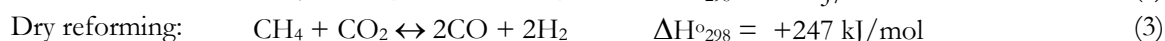
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Hydrogen has been an important commodity in many industries. For chemical and petrochemical industries, it is a feedstock for production of various chemicals such as hydrogen peroxide, ammonia and methanol. For refinery, it is used in a hydrotreating process to achieve the required high-quality products from poor-quality crude. Food processing industry also uses hydrogen for hydrogenation of fats and oils. Nowadays, hydrogen is considered a clean fuel for transportation and stationary power generation using fuel cell technology. Because hydrogen is not naturally available, a fuel processing technology is essential to convert many possible fuels (e.g. biomass, hydrocarbons and alcohols) to hydrogen. Among the various fuels, methane is a promising source of hydrogen production as it is a main component in natural gas and renewable biogas. There are many possible reaction routes to generate hydrogen from methane as summarized below:



Steam reforming (Eq. (1)) is performed at a high temperature to favor the production of hydrogen and carbon monoxide. Partial oxidation (Eq. (2)) is an exothermic reaction and converts methane to hydrogen by reacting with limited oxygen to avoid the complete oxidation that generates steam and carbon dioxide products. Autothermal reforming is a promising process combining the steam reforming and partial oxidation. It offers several advantages such as high energy efficiency, no requirement of an external heat source (and thus complicated heat exchangers) and avoidance of catalyst deactivation. Steam reforming, partial oxidation and autothermal reforming have been the dominant industrial routes for hydrogen production for several decades. Since these reforming processes produce large amounts of carbon monoxide, a water gas shift reactor is usually installed after the reforming section to further convert carbon monoxide by reacting with steam to hydrogen and carbon dioxide. Methane dry reforming (Eq. (3)) is an interesting reaction for converting both greenhouse gases (methane and carbon dioxide) to synthesis gas with low hydrogen-to-carbon monoxide ratio suitable for further synthesis of various chemicals. The main obstacle to the industrial implementation is due to the catalyst deactivation from carbon deposition. Methane decomposition (Eq. (4)) is an alternative route for production of CO_x -free hydrogen suitable for a low temperature fuel cell.

To date, there have been many research and development efforts to improve the technologies for hydrogen production from methane. The direction can be broadly classified into (i) new catalyst development, (ii) changing reaction field and (iii) applications of multifunctional reactors and/or novel operation mode. Various new metal catalyst compositions, supports and promoters as well as preparation methods are being developed with the aim of achieving the high catalytic activity, selectivity and stability [1,2]. Catalyst deactivation especially from carbon deposition is a major problem of most reforming catalysts. Presently, carbon materials are being investigated as potential catalysts for the decomposition and dry reforming of methane to achieve the operation without getting deactivated by carbon. They also offer certain advantages over metal-based catalysts such as (i) low cost, availability and durability, (ii) high temperature resistance, (iii) tolerance to sulphur and other potentially harmful impurities and (iv) no need for catalyst regeneration by burning carbon off the surface [3]. Controlling a reaction field is another option for enhancement of hydrogen production. A plasma-assisted reforming technology for hydrogen production has been investigated since early 1990s. It offers several potential benefits including fast startup, compatibility with a broad range of hydrocarbons, less catalyst sensitivity to impurities in feed, compactness and synergism enhancing hydrogen production [4]. A concept of multifunctional reactor and novel operation mode has been applied and made significant progresses to the hydrogen production technology. Removal of hydrogen from the reaction mixture in a palladium-based membrane reactor (Fig. 1a) helps shift the reforming reaction forward, enabling the reaction to operate at a lower temperature which alleviates several problems associated with catalyst fouling, high energy demand and requirement of expensive materials. In addition, ultra-pure hydrogen can be generated due to a good characteristic of the highly selective palladium membrane. The main obstacles inhibiting the commercial implementation of this technology are arisen from a high cost of palladium and poor durability from several problems such as hydrogen embrittlement. Current research and development have focused on reducing the amount of palladium by using its alloys, fabrication of palladium membrane, and design and optimization of a compact membrane reactor [5,6]. Application of a sorption-enhanced reaction concept has been successfully

demonstrated to the hydrogen production via methane steam reforming [7]. The reaction is promoted by the selective adsorption of carbon dioxide on an acceptor such as calcium oxide and hydrotalcite. Other benefits are realized on the efficient heat integration as the exothermic heat of adsorption can be directly utilized for the endothermic steam reforming. In addition, the catalyst is less susceptible to fouling due to the presence of a lower CO_x content in the reaction mixture. Generally, this reactor is operated under a periodic mode. When the adsorbent nearly reaches its sorption capacity, the reactor is switched to a regeneration mode to desorb carbon dioxide, allowing subsequent CO_2 utilization or sequestration to relieve a global warming problem. It is also possible to operate the system under continuous mode by using two reactors - one as the reformer and the other as the regenerator - with circulation of the adsorbent (Fig. 1b). Another technology based on the similar concept is a chemical looping reforming (Fig. 1c). A solid oxygen carrier is employed to transfer oxygen from air to a fuel for reforming reaction [8]. For both the technologies, the major challenge is on the development of suitable materials for the process as their performance trends to deteriorate after many repeated cycles due to many possible problems associated with gas impurities, carbon deposition, particle agglomeration and so on. In addition, the process design and optimization are also rather complicated.

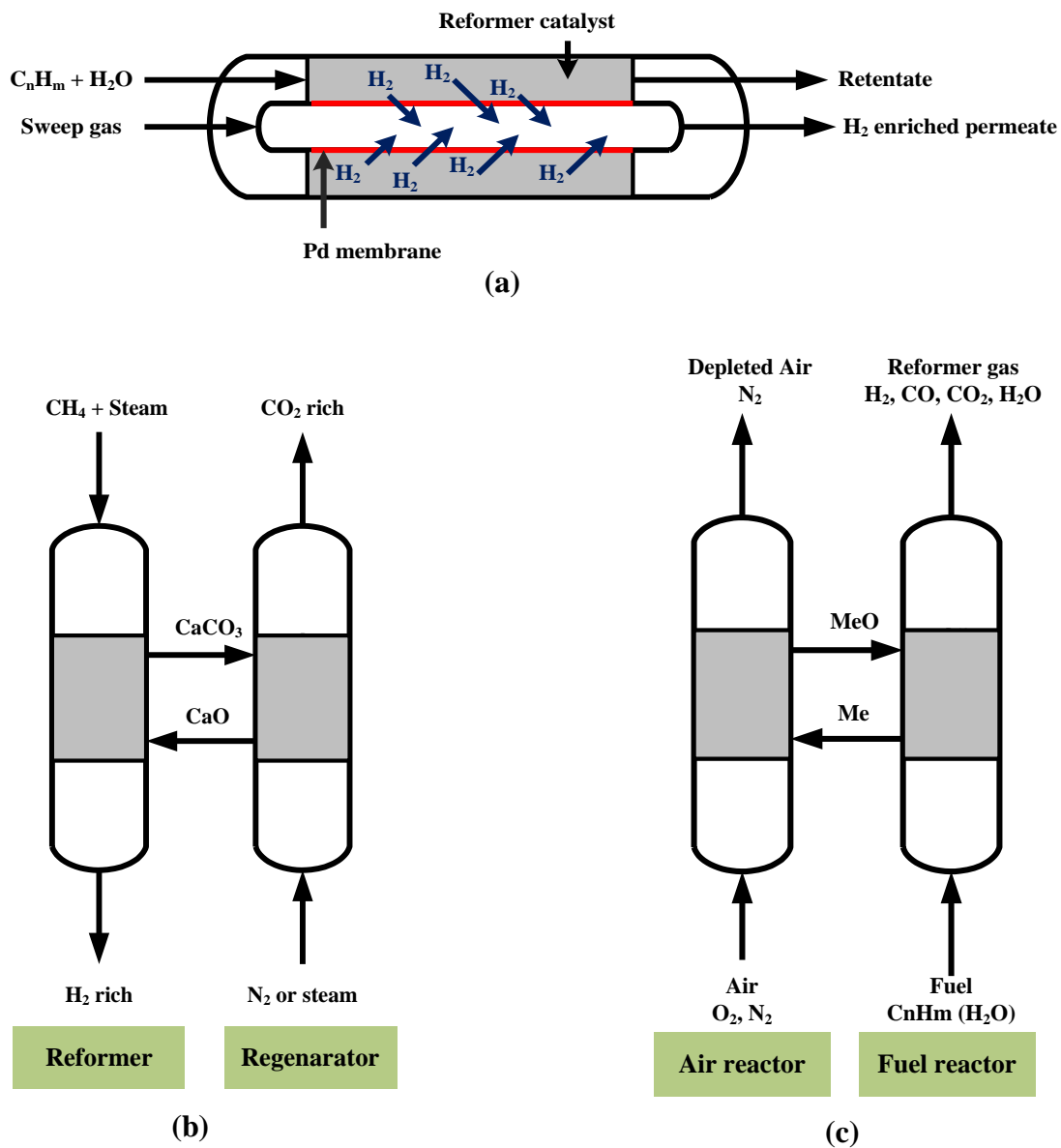


Fig. 1. Multifunctional reactors for hydrogen production: (a) Pd membrane reactor; (b) sorption enhanced methane steam reforming; (c) chemical-looping reforming.

It is obvious that there are many promising technologies for hydrogen production. The key driver for the research and development efforts is from the advancement of fuel cell technology. Most of the technologies aforementioned have been successfully demonstrated in pilot-scale processes; however, there are still many important issues that need to be accomplished before the commercialization. They are, for example, material stability, cost, compact reactor and process design and scale up. It is expected that in the near future these technologies become industrially competitive with the conventional reformers.

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