



Advances in reforming and partial oxidation of hydrocarbons for hydrogen production and fuel cell applications



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ABSTRACT

One of the most attractive routes for the production of hydrogen or syngas for use in fuel cell applications is the reforming and partial oxidation of hydrocarbons. The use of hydrocarbons in high temperature fuel cells is achieved through either external or internal reforming. Reforming and partial oxidation catalysis to convert hydrocarbons to hydrogen rich syngas plays an important role in fuel processing technology. The current research in the area of reforming and partial oxidation of methane, methanol and ethanol includes catalysts for reforming and oxidation, methods of catalyst synthesis, and the effective utilization of fuel for both external and internal reforming processes. In this paper the recent progress in these areas of research is reviewed along with the reforming of liquid hydrocarbons, from this an overview of the current best performing catalysts for the reforming and partial oxidizing of hydrocarbons for hydrogen production is summarized.

1. Introduction

Fuel cells are electrochemical energy conversion devices that are used to convert the chemical energy stored in chemical fuels directly to electrical energy [1–5]. They offer many advantages such as high efficiency, low emissions, system compactness and environmental benefits when compared to conventional energy conversion technologies. Among the various types of fuel cells, solid oxide fuel cells (SOFCs) are well recognized due to advantages such as fuel flexibility, high tolerance to impurities in the fuel and not requiring expensive noble metal catalysts [6–14]. In conventional SOFCs, Ni-yttria stabilized zirconia (YSZ) is used as the anode and hydrogen is used as the fuel [15–17]. When this Ni-YSZ anode operated using hydrocarbon fuels instead of hydrogen then an efficiency increase can be seen at the system level [18–20]. However, when the Ni-YSZ anode is exposed to hydrocarbon fuels then carbon deposition will occur leading to the system failure [20–22]. When raw fuels, such as diesel, natural gas, and methanol are used, a fuel processor is needed to reform the hydrocarbons into a hydrogen rich gas for the fuel cell to perform the electrochemical conversion [23,24]. This has led to a great interest in converting hydrocarbons into hydrogen. Fuel processing technologies for high temperature fuel cells involve the conversion of hydrogen rich fuels such as gaseous hydrocarbons, gasoline, ammonia, or methanol into a hydrogen rich stream [25,26].

The development of converting hydrocarbon fuels to hydrogen-rich gas products generally fall in one of following processes: steam reforming (SR), auto thermal reforming (ATR), dry reforming (DR), partial oxidation (POX) or a combination of two or more [27]. In spite of their advantages, each of these processes is limited due to factors such as design, fuel and operating temperature. A range of fuel cell systems and common fuel reforming methods have been reviewed by Larminie and Dicks [28]. Thermodynamical analyses of the reforming processes for producing fuel cell feeds of the necessary quality using different fuels have been carried out. In 2006, reforming catalysts for hydrogen generation in fuel cell applications was reviewed by Cheekatamarla et al. [27] There is currently a wide selection of potential fuel reforming catalysts receiving research attention. When investigating a fuel reforming catalyst for fuel cell applications the critical consideration are weight, size, activity, cost, transient operations, versatility to reform different fuels/compositions, catalyst durability and fuel processor efficiency. A suitable catalyst for fuel reforming will catalyze the reaction at low temperatures, is resistant to coke formation, and is tolerant of different concentrations of poisons (e.g. sulphur, halogens, heavy metals, etc.) for an extended period of time. The challenges and opportunities of various fuel reforming technologies for applications in low and high-temperature fuel cells have been previously reviewed [27,29–31]. In previous papers the various steps involved in the generation of fuel cell grade hydrogen with respect to catalyst development

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has been discussed [32–35]. A couple of excellent reviews on CO₂ reforming and partial oxidation of methane are also available [36,37]. The production of hydrogen from steam reforming of ethanol and glycerol was also reviewed in 2005 and 2009 respectively [38,39]. The goal of the present paper is to review and discuss recent progress in the catalyst development, particularly, steam reforming and partial oxidation catalysts and their ability to generate hydrogen from different fuel sources for fuel cell applications. The focus will be on transition metals supported on mixed metal oxides and perovskites oxides. This paper surveys four key processes in H₂ and syngas production technologies in the following sections, including Section 2 internal reforming for hydrogen production in solid oxide fuel cells, Section 3 – external reforming for hydrogen production (steam reforming of methane, partial oxidation of methane, CO₂ Reforming of methane) Section 4 – reforming of liquid hydrocarbons, Section 5 poisoning of catalyst and in Section 6 – reforming and partial oxidation catalysts for direct hydrocarbon solid oxide fuel cells. A summary section is also provided with descriptions on challenges and future work (Section 7), followed by the conclusion section. Some key papers in previous studies are also cited.

2. Internal reforming for hydrogen production

Among the various types of fuel cell systems, SOFCs can offer more fuel flexibility by internal reforming of hydrocarbon fuels such as methane, propane, ethanol and natural gas, at the anode [40–42]. Among the various hydrocarbon fuels, methane and propane are the most widely available with vast supply worldwide. By internally reforming hydrocarbon fuels in the SOFCs then an increase in efficiency can be observed as well as simplifying the integration of the system. For example, Eric et al. [43], reported that the efficiency of the internal reforming is 8% higher, compared to the external reforming in the same SOFC system. Simplified thermal management and higher fuel cell performance can be achieved when internally reforming of the fuel is used over external reforming. Also, the internal reforming process in SOFCs can be operated at low steam/carbon ratios compared to the external reforming process. When carrying out internal reforming in a SOFC, it should be noted that the conventional Ni based anode cermet will display poor catalytic activity towards the hydrocarbon and steam/CO₂ reforming due to carbon deposition at the Ni cermet anode. The catalytic modification of conventional Ni cermet anode for direct internal reforming is more useful than the identification of new anodes which are tolerant to hydrocarbon fuels. In order to improve the reforming reaction of the hydrocarbons while also improving the stability of the Ni cermet anode against carbon deposition a layer of reforming catalyst can be deposited over the Ni anode. Under the direct internal reforming conditions, hydrocarbon fuels with steam/CO₂ are passed through the catalytic functional layer, where the fuel is converted into syngas before it reaches the anode. The catalytic layer requires particular properties such as a high catalytic activity towards hydrocarbon reforming and high resistance against carbon deposition. Thus the greater partial reforming reactions occur at the functional catalyst layer with the hydrocarbon fuels converted into syngas as they reach the cermet anode.

Zhan et al. [19] first demonstrated the use of Ru-CeO₂ catalyst as a direct internal reforming catalyst with the Ni cermet anode. They applied a porous Ru-CeO₂ catalyst layer against the Ni cermet anode side of the fuel cell. This porous Ru-CeO₂ catalyst layer is used to internally reform the hydrocarbons into syn-gas. Sun et al. studied the effect of morphological features of CeO₂ catalyst on direct internal reforming the hydrocarbons [44]. The performance of the fuel cell with mesoporous flower like Ru-CeO₂ catalyst shows a power density up to 654 mW cm⁻² at 600 °C [45]. Klein et al. studied the Ir (0.1 wt%)–CeO₂ catalyst on Ni-YSZ cermet anode in CH₄ fuel [46,47]. Fig. 1 shows the anodic gas phase composition compared to current of the cell in pure methane fuel at 900 °C. H₂ and CO are the only major products for the internal reforming reaction occurring at the catalyst layer. Fuel cells

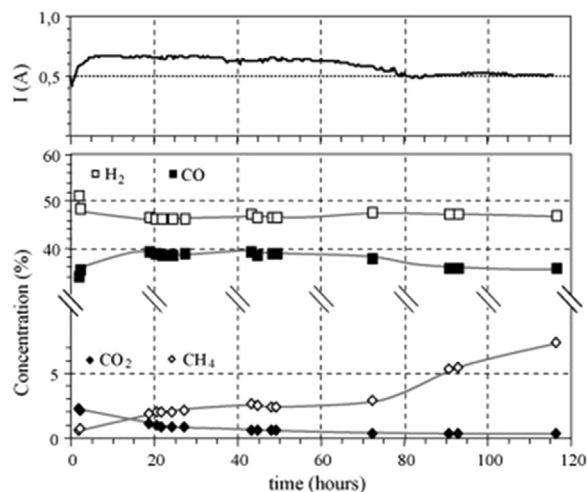


Fig. 1. Evolution as a function of time of the anodic gas phase composition compared to the current of the cell; the cell was operated at $V = 0.6$ V in pure CH₄ with a total flow rate of 4 sccm; dashed line represents the levels measured at OCV in diluted H₂ at 900 °C [46].

with an Ir-CeO₂ catalyst show stable fuel cell operation for 120 h in methane at 900 °C and 0.6 V yields a current density of about 100 mA cm⁻² [46]. However, it has been noted that the methane concentration gradually increased after 70 h (Fig. 1) indicating that the reforming or partial oxidation activity of the anode started to decrease at this time, however, the fuel cell performance was not affected. One of the possible reasons for this may be due to other mechanisms, such as the direct oxidation of methane playing an important role in retaining the stable current.

Wang et al. [48] studied the effect of Ru loading and their catalytic activities on Al₂O₃ supported catalysts for internal reforming of methane by partial oxidation, steam reforming and CO₂ reforming under SOFC operating conditions. They found that 1 wt% Ru-Al₂O₃ catalyst shows insufficient catalytic activity towards methane reforming. A 3 wt% Ru-Al₂O₃ catalyst shows an outstanding stability and a good thermal stability with the Ni-YSZ anode. Fig. 2 shows the electrochemical performance of 3 wt% Ru-Al₂O₃ anode in H₂, methane-oxygen, methane-steam and methane-CO₂ gas mixtures. At 850 °C, the fuel cell using a methane-oxygen mixture shows a peak power density of 1006 mW cm⁻², while the same fuel cell shows 1038 mW cm⁻² in pure H₂.

It has been found that addition of metal oxides can improve coke resistance property. Wang et al. [49–51] also studied the effect of promoters Li₂O, La₂O₃, CaO, CeO₂, Pr₂O₃, Sm₂O₃ and Gd₂O₃ on the Ni-Al₂O₃ catalyst with the aim of improving its coking resistance during fuel cell operation with methane fuels. Among the various promoters, LiLaNi/Al₂O₃ showed the best catalytic activity and stability compared to LaNi-Al₂O₃ and LiNi-Al₂O₃ catalysts. Lee et al. [52] studied the effect of pore formers in the Ni-Fe anode reforming catalyst on Ni-YSZ fuel cell. The fuel cells containing pore formers (10 wt% carbon black (HB170)) in the Ni-Fe catalyst layer exhibited the highest power density, when compared to the fuel cell containing Ni-Fe catalyst layer without pore formers. It should be noted that some oxides such as CaO, Li₂O may react with CO₂ to form stable carbonate thereby losing their promoting effects. Liao et al. [53], studied the doped ceria Ce_{0.8}Zr_{0.2}O₂ catalyst for direct internal reforming of ethanol. The high oxygen storage capacity, thermal stability and the ability of doped ceria to promote the water gas shift reaction makes Ce_{0.8}Zr_{0.2}O₂ a good catalyst for internal reforming. The catalytic activity is also related to the synthesis process. Liao et al. used different synthesis processes to prepare the Ni-Ce_{0.8}Zr_{0.2}O₂ catalyst. Ni-Ce_{0.8}Zr_{0.2}O₂ catalyst prepared by the glycine nitrate process (GNP) exhibited the best catalytic properties compared to the Ni-Ce_{0.8}Zr_{0.2}O₂ catalyst prepared by the infiltration method. Above 600 °C, both the Ni-Ce_{0.8}Zr_{0.2}O₂ catalysts show a high and

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