



Reforming of natural gas using coking-resistant catalyst for fuel cell system applications

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HIGHLIGHTS

- ▶ α -Al₂O₃ is a more stable catalyst support than γ -Al₂O₃.
- ▶ The Pt/CeO₂/ α -Al₂O₃ catalyst is able to effectively eliminate coking problem.
- ▶ The CeO₂ coating layer provides excellent coking resistance for the catalyst.
- ▶ The CeO₂ coating layer also prevents catalyst from being pulverized.

ARTICLE INFO

Article history:

Received 28 June 2012

Received in revised form

24 August 2012

Accepted 27 August 2012

Available online 10 September 2012

Keywords:

Reforming catalyst

Catalyst support

Coking-resistance

Natural gas reforming

Autothermal reforming

Solid oxide fuel cell

ABSTRACT

A coking-resistant catalyst prepared using a novel catalyst support is characterized and its performance on reforming of natural gas for fuel cell system applications is investigated. Two key issues, i.e., the stability of catalyst under the reforming environment and deposition of carbon on the catalyst surfaces leading to deactivation, have to be resolved. The reforming operations are performed using a modified external autothermal reforming (ATR) approach. Desulfurized natural gas is used as a feedstock to avoid catalyst poisoning and air is exploited as an oxidant. It is found that the reforming catalyst is able to remain stable and free from pulverization at the desired operating conditions when α -Al₂O₃ is employed as a catalyst support in place of the commonly used γ -Al₂O₃ counterpart. In addition, the ceria (CeO₂)-assisted Pt catalyst coated on the α -Al₂O₃ support, i.e., Pt/CeO₂/ α -Al₂O₃, is able to significantly eliminate the coking problem with a CH₄ conversion rate >99% and a generated H₂ concentration ~62% at 1073 K. A reaction mechanism is proposed to elucidate the coking-resistance of the catalyst, which also accounts for the stability of the catalyst. The reforming catalyst has been tested continuously for 2400 h and is still able to maintain a good operating condition.

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1. Introduction

Solid oxide fuel cells (SOFCs) have been intensively investigated and developed for uses as an integral part of distributed power systems due to their high efficiencies, clean emissions, and operational quietness. Particularly, SOFC micro-combined heat and power (CHP) systems (<2 kW) for residential applications have become a focus of attention recently. This is due to high power efficiency (~60%) and high overall energy efficiency (~90%) with a triple function of power generating, heating, and cooling of the SOFC micro-CHP system, which is of special interest to the users. With the oil price rising to sky high and the need of substantial

reduction in carbon emissions to the atmosphere, the demands for such high efficiency, clean power generating devices are ever-increasing.

Although a variety of fuels, such as hydrogen, natural gas, methane, alcohols, etc., can be applied to SOFCs, hydrogen gives the best performance of all. However, hydrogen gas needs to be generated by a suitable means to sustain the supply. Therefore, reforming of alternative fuels on site to provide hydrogen-rich gas for the SOFC stack is a common practice. Among them, reforming of natural gas, or methane [1,2], is the most promising one due to its abundance and easy supply. Natural gas contains mainly methane (>90%). With the aid of proper catalysts, methane undergoes catalytic reactions at high temperatures (e.g., >973 K) to generate hydrogen-rich gas, which can be directly applied to the SOFC stack.

The reforming catalyst must be stable and have high catalytic performance. In addition, it must be coking-resistant to ensure uninterrupted operation of the SOFC power system. There are three

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main reforming approaches, i.e., steam reforming (SR), partial oxidation reforming (POR), and autothermal reforming (ATR), which have been developed and employed in the fuel cell systems [3,4]. Briefly, SR is the reaction of fuel with steam to generate mainly carbon monoxide and hydrogen, i.e., syngas. It is an endothermic reaction and, therefore, external supply of heat to sustain the reforming reaction is required. POR is the reaction of fuel with a controlled amount of air (oxygen) to generate syngas. The reaction is exothermic and the generated heat is used to sustain the reforming reaction. Finally, ATR is the reaction of fuel with both steam and air (oxygen) to generate syngas. The reforming reaction is designed to be thermally neutral. In the present case, the reformer is aimed to be simple and compact for fuel cell system applications. The one-stage ATR approach [5–25], basically a combination of both SR and POR processes, has higher fuel efficiency than POR and better dynamic start-up capability than SR [4]. It also has the advantages of operating in a POR mode to quickly start up the reformer and the fuel cell stack as well as operating in an SR mode to generate more hydrogen if needed. Therefore, it is first chosen for carrying out performance tests.

Depending on the feedstock and the reforming approach used, a variety of catalysts, such as nickel- and platinum-based catalysts supported mainly on gamma alumina ($\gamma\text{-Al}_2\text{O}_3$), have been developed for such purposes [26–34]. However, the catalyst becomes less effective as unwanted side reactions may occur. A major cause of catalyst deactivation in reforming catalysts is coking [35–37], i.e., carbon is deposited on the surface of the catalyst resulting in catalyst failure. To solve this formidable problem, perhaps the best way is resorting to the use of effective coking-resistant catalysts. One of the most commonly employed approaches is exploiting a metal oxide, such as CeO_2 , as a promoter [36–38] to a metal catalyst, e.g., nickel. This approach leads to the development of advanced reforming catalysts with better coking resistances and reforming performances [12]. Another problem has to be dealt with is the stability of the catalyst support. It was found from our previous experiments that the reforming at high operating temperature ($\sim 1073\text{ K}$) for natural gas can easily cause breakdown and pulverization of the reforming catalyst, which generally uses low-temperature formed $\gamma\text{-Al}_2\text{O}_3$ support due to its inexpensiveness and porous structure. It is speculated that excessive

accumulation of the deposited carbon in such porous structure might cause structural failure at high reforming temperatures. Thus, more robust and stable catalyst supports that can stand the reforming environment are urgently needed to be explored.

At present, reforming of natural gas is still a topic of intensive investigation for fuel cell system applications. Since the reformer investigated is a small-scale device, it must have somewhat different operating approaches from those of the industrial large-scale systems. In this study, a modified external autothermal reforming approach, using water and air instead of steam and pure oxygen, is employed. The developed small reformer is intended to be integrated with a 1 kW SOFC micro-CHP system.

2. Experimental

2.1. Preparation and characterization of reforming catalysts

The $\gamma\text{-Al}_2\text{O}_3$ species is purchased from Alpha Aesar in a form of $3.2 \times 10^{-3}\text{ m}$ tablet having a specific surface area of $1.75 \times 10^5\text{ m}^2\text{ kg}^{-1}$ and containing 3% carbon. To obtain $\alpha\text{-Al}_2\text{O}_3$, the $\gamma\text{-Al}_2\text{O}_3$ is put in an oven and blown with air. The temperature is then increased at a rate of $8.33 \times 10^{-2}\text{ K s}^{-1}$ ($5\text{ }^\circ\text{C min}^{-1}$) to 1473 K followed by sintering for 6 h. Finally, the temperature is decreased at a rate of $8.33 \times 10^{-2}\text{ K s}^{-1}$ to room temperature. The CeO_2 -assisted Pt catalyst coated on $\alpha\text{-Al}_2\text{O}_3$ support, i.e., $\text{Pt/CeO}_2/\alpha\text{-Al}_2\text{O}_3$, is prepared using the procedure as illustrated in Fig. 1, and the $\text{Ni/CeO}_2/\alpha\text{-Al}_2\text{O}_3$ catalyst is prepared following a procedure similar to that of the Pt-based counterpart.

Characterizations of the prepared alumina supports and alumina-supported catalysts are carried out. The alumina supports are characterized using X-ray diffraction (XRD) (Bruker, D8 ADVANCE) technique to examine their crystalline structures, and both species are characterized using BET method to measure their surface areas. In addition, the catalyst layers are examined using a scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) instrument (JEOL, JSM-6510) to characterize the surface structures and elemental compositions. The morphology of the $\text{Pt/CeO}_2/\alpha\text{-Al}_2\text{O}_3$ catalyst layer before and after reforming operation is illustrated using transmission electron microscopy (TEM).

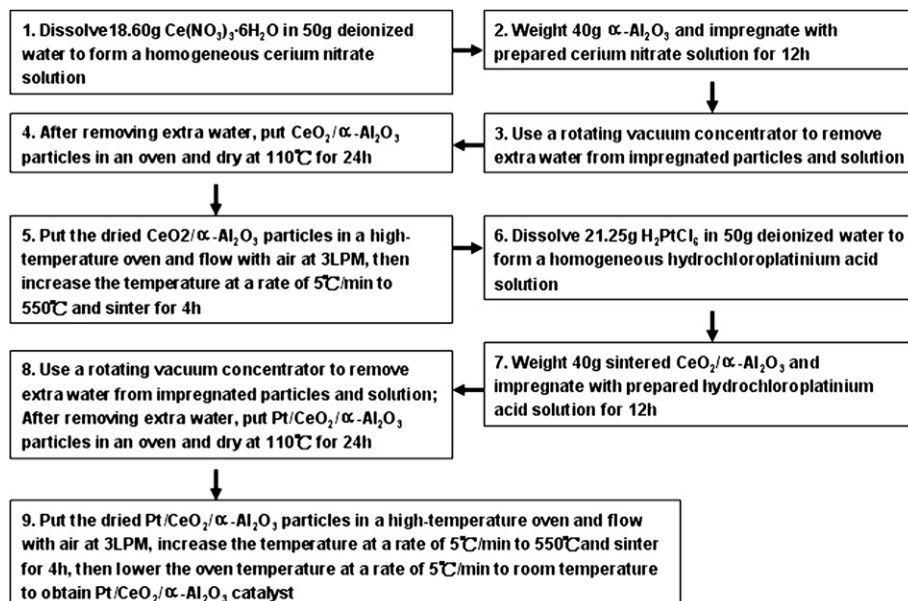


Fig. 1. Illustration of preparation procedure for $\text{Pt/CeO}_2/\alpha\text{-Al}_2\text{O}_3$ catalyst.

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