Available online at www.sciencedirect.com

ScienceDirect

Applied Catalysis A: General 320 (2007) 105–113

APPLIED CATALYSIS A: GENERAL

www.elsevier.com/locate/apcata

Catalytic steam reforming of dimethyl ether (DME) over high surface area Ce–ZrO_2 at SOFC temperature: The possible use of DME in indirect internal reforming operation (IIR-SOFC)

N. Laosiripojana [a,*], S. Assabumrungrat [b]

[a] *The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand*
[b] *Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Chulalongkorn University, Bangkok 10330, Thailand*

Received 14 September 2006; received in revised form 14 December 2006; accepted 24 December 2006

Abstract

This study was aimed at developing a suitable reforming catalyst for later application in an indirect internal reforming solid oxide fuel cell (IIR-SOFC) fuelled by dimethyl ether (DME). It was found that, at temperature higher than 800 °C, DME decomposed homogeneously, producing CH_4 and CH_3OH with small amount of CO, CO_2, and H_2. High surface area Ce–ZrO_2 can reform DME with steam efficiently at 900 °C, producing high contents of H_2, CO, and CH_4 without the presence of CH_3OH in the product gas. The combination use of Ce–ZrO_2 (as a pre-reforming catalyst) and Ni/Al_2O_3 in the single unit was proven to significantly improve the reforming performance. According to this combination, the role of Ce–ZrO_2 is to first decompose CH_3OH and some CH_4 generated from the homogeneous decomposition of DME, while the role of Ni/Al_2O_3 is to reform CH_4 left from the pre-reforming section and to maximize the yield of H_2 production.

As another approach, IIR-SOFC model was studied using an annular ceramic reactor, in which DME initially reacted with steam on Ce–ZrO_2 + Ni/Al_2O_3 at the inner side of the reactor and then Ni/YSZ at the outer side. The stability and the yield of hydrogen production over this configuration were considerably higher than those of systems packed with single Ce–ZrO_2, single Ni/Al_2O_3, and without the filling of catalyst. In addition, the degree of carbon formation on the surface of Ni/YSZ was significantly low. The successful development of this reforming pattern improves the efficiency of IIR-SOFC fueled by DME by eliminating the requirement of an external reforming unit installation.

Keywords: Indirect internal reforming; Dimethyl ether; Ce–ZrO_2; Solid oxide fuel cell

---

1. Introduction

Solid oxide fuel cell (SOFC) is an efficient electrochemical device that converts chemical energy to electrical energy with higher efficiency and lower pollutant emission compared to conventional processes [1]. H_2 and CO are the primary fuels for SOFC. Nevertheless, due to high operating temperature of SOFC (700–1100 °C), it is known that some fuels (i.e. CH_4) can be directly fed to SOFC stacks; this operation is called a direct internal reforming SOFC (DIR-SOFC). According to this operation, the fuels are reformed at the anode producing H_2 and CO, which are electrochemically consumed for generating electricity simultaneously. An advantage of DIR-SOFC is that the H_2 consumption by the electrochemical reaction could promote the reforming or conversion of fuels at the anode side and consequently results in high conversion and efficiency [2].

DIR-SOFC operation requires an anode material that has good catalytic reforming and electrochemical reactivities. Ni/YSZ is the most common SOFC anode material due to its well-fitted properties for SOFC design requirement and its low cost compared with other supported metals (e.g. Co, Pt, Ru, and Rh). In addition, this material provides necessary catalytic reforming activity required for the DIR-SOFC operation. The nickel content for Ni/YSZ anode is usually 40–60% in order to match the thermal expansion of YSZ [3]. The major difficulty of DIR-SOFC operation over Ni/YSZ is the possible formation of carbon species on the surface of Ni due to the cracking of hydrocarbons. This formation could hinder gas access and

---

* Corresponding author. Tel.: +66 2 8729014; fax: +66 2 8726736.
E-mail address: navadol_l@jgsee.kmutt.ac.th (N. Laosiripojana).

0926-860X/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2006.12.018

degrade anode performance by blocking the catalyst active sites, which resulted in the loss of cell performance and poor durability. Another alternative internal reforming operation is an indirect internal reforming (IIR-SOFC). By this operation, the reforming reaction takes place at a reformer located in close thermal contact with the anode side of SOFC. IIR-SOFC gives the advantage of good heat transfer between the reformer and the fuel cell and is expected to provide an autothermal operation. In addition, unlike DIR-SOFC, the reformer part and the anode side for IIR-SOFC operation are operated separately. Therefore, the catalyst for reforming reaction at the reformer part and the material for electrochemical reactions at the anode side of fuel cell can be optimized individually, preventing the possible degradation of anode from the carbon deposition.

Focusing on the fuel selection, methane is currently the major fuel for SOFC due to its well-developed supporting system and cost effectiveness. Nevertheless, the use of dimethyl ether (DME) should also be possible when operated as an internal or in-stack reforming. DME has several advantages; it is harmless and does not cause ozone layer destruction, and it is easy to handle like LPG. The approach in this work is to develop an indirect internal reforming operation that can reform DME efficiently at SOFC temperatures, 900 °C. The successful development of this operation would eliminate the requirement of the external reformer installation, making SOFC fueled by DME more efficient and attractive. Previously, hydrogen production from the reforming of DME has been studied over acid catalysts and Cu-based catalysts by several researchers; however, most of them have investigated the reforming of DME at low temperature [4–9].

In the present work, ceria-based catalyst was selected as the catalyst for the steam reforming of DME at SOFC operating temperature. Ceria-based catalysts have been commonly applied as catalysts in a wide variety of reactions involving oxidation or partial oxidation of hydrocarbons (e.g. automotive catalysis). A high oxygen mobility (redox property) [10], high oxygen storage capacity (OSC) [11], strong interaction with the supported metal (strong metal–support interaction) [12] and the modifiable ability [13] render this material very interesting for catalysis. Importantly, the reactivity toward methane steam reforming with high resistance toward carbon deposition over ceria has been observed [14–17]. Doped ceria with Zr (Ce–ZrO_2) has been reported to improve the specific surface area, oxygen storage capacity, redox property, thermal stability and catalytic activity. These benefits were associated with enhanced reducibility of cerium (IV) in CeO_2–ZrO_2 due to the high O^{2-} mobility inside the fluorite lattice. The reason for high mobility might be related to the lattice strain, which is generated by the introduction of a smaller isovalent Zr cation into the CeO_2 lattice (Zr^{4+} has a crystal ionic radius of 0.84 Å, which is smaller than 0.97 Å for Ce^{4+} in the same co-ordination environment) [18]. Therefore, Ce–ZrO_2 was selected for study in the present work. Furthermore, the benefit of applying Ce–ZrO_2 together with conventional Ni/Al_2O_3 was also studied.

As a next step, in order to study the possible use of Ce–ZrO_2 in IIR-SOFC, an annular ceramic reactor was designed and constructed. Details of this reactor configuration will be described in Section 2.2. DME and steam were fed into this annular reactor packed with Ce–ZrO_2 and/or Ni/Al_2O_3, as reforming catalysts, and Ni/YSZ, an anode material of SOFC. The stability and reforming reactivity toward this operation was investigated compared to those without the use of reforming catalysts (DIR operation).

2. Experimental

2.1. Material preparation and characterization

Ce–ZrO_2 with different Ce/Zr molar ratios were prepared by co-precipitation of cerium nitrate ($Ce(NO_3)_3 \cdot H_2O$), and zirconium oxychloride ($ZrOCl_2 \cdot H_2O$) (from Aldrich). The ratio between both solutions was altered to achieve Ce/Zr molar ratios of 1/3, 1/1 and 3/1. It should be noted that aqueous solution of 0.1 M cetyltrimethylammonium bromide solution (from Aldrich) was also added in the cerium nitrate and zirconium oxychloride solution as a cationic surfactant. Our previous work reported that the preparation of ceria-based material by this surfactant-assisted method can achieve high surface area and high thermal stability due to the incorporation of surfactants during preparation, which reduces the interfacial energy and eventually decreases the surface tension of water contained in the pores [14,19,20].

In the present work, the molar ratio of ([Ce] + [Zr])/[cetyltrimethylammonium bromide] was kept constant at 0.8. The solid solution was formed by mixing 0.1 M of metal salt solution with 0.4 M of urea at a 2:1 volumetric ratio. This solution was stirred by a magnetic stirrer (100 rpm) for 3 h, and the precipitate was filtered and washed with deionised water and ethanol to prevent an agglomeration of the particles. It was dried overnight in an oven at 110 °C, and then calcined in air at 1000 °C for 6 h. Fig. 1 shows the SEM micrographs of Ce–ZrO_2 (with Ce/Zr = 3/1) synthesized by the above surfactant-assisted method (1a), compared to that synthesized by typical co-precipitation method (1b) (without the filling of cetyltrimethylammonium bromide solution). It is clear that the particle size of Ce–ZrO_2 synthesized by the surfactant-assisted method (Ce–ZrO_2 (high surface area; HSA)) is significantly smaller than that synthesized by typical co-precipitation method (Ce–ZrO_2 (low surface area; LSA)).

Ni/Al_2O_3 catalysts were prepared by impregnating γ-Al_2O_3 with $Ni(NO_3)_2$ solution (Aldrich). The catalysts were reduced with 10%H_2/He before use. After reduction, the catalysts were characterized with several physicochemical methods. The weight content of Ni in Ni/Al_2O_3 was determined by X-ray fluorescence (XRF) analysis. The reducibility and dispersion percentages of nickel were measured from temperature programmed reduction (TPR) with 5% H_2 in Ar and temperature programmed desorption (TPD), respectively. The catalyst specific surface areas were obtained from BET measurements, which were carried out before and after calcination in order to determine its changes. All physicochemical properties of the synthesized catalysts are presented in Table 1. It should be noted that, after treatment, the degree of oxygen storage capacity (OSC) and redox reversibilities of all