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Reactivity of Ce-ZrO₂ (doped with La-, Gd-, Nb-, and Sm-) toward partial oxidation of liquefied petroleum gas: Its application for sequential partial oxidation/steam reforming

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ABSTRACT

Ce-ZrO₂ was found to have useful partial oxidation activity under moderate temperatures. It converted liquefied petroleum gas (LPG) to H₂, CH₄, CO and CO₂ with small amounts of C₂H₆ and C₂H₄ formations depending on the operating temperature and provided significantly greater resistance toward carbon deposition compared to conventional Ni/Al₂O₃. The doping of La, Sm and Gd over Ce-ZrO₂ considerably improved catalytic reactivity, whereas Nb-doping reduced its reactivity. It was found that the impact of doping element is strongly related to the degrees of oxygen storage capacity (OSC) and/or lattice oxygen (O_l^x) of materials. Among all catalysts, La-doped Ce-ZrO₂ was observed to have highest OSC value and was the most active catalyst. Above 850 °C with inlet LPG/O₂ molar ratio of 1.0/1.0, the main products from the reaction over La-doped Ce-ZrO₂ were H₂, CH₄, CO, and CO₂.

Practical application was then proposed by applying La-doped Ce-ZrO₂ as primary oxidative catalyst for sequential partial oxidation/steam reforming of LPG (by using Ni/Al₂O₃ as the steam reforming catalyst). At 850 °C, this coupling pattern offered high H₂ yield (87.0–91.4%) without any hydrocarbons left in the products indicating the complete conversion of LPG to syngas. H₂ yield from this system was almost identical to that observed from the typical autothermal reforming over Rh/Al₂O₃; hence it could efficiently replace the requirement of expensive noble metal catalysts to reform LPG properly.

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1. Introduction

Hydrogen-rich fuel is a major fuel for Solid Oxide Fuel Cell (SOFC), which can be produced readily from the reactions of several hydrocarbon fuels i.e. methane, methanol, ethanol, liquefied petroleum gas (LPG), gasoline and other oil

derivatives with oxygen-containing co-reactant i.e. oxygen, steam, and carbon dioxide. Partial oxidation and steam reforming as well as the combination of both reactions (as called autothermal reforming) have been known as feasible processes to produce hydrogen-rich fuel from several hydrocarbons [1,2]. Steam reforming is probably the most common

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method for producing hydrogen in chemical process industry [1], however, it has a disadvantage of slow start-up, which makes it more suitable for a stationary system rather than for a mobile system [2]. Recently, catalytic partial oxidation [3–6] and autothermal reforming [7,8] appear to have attracted much interest. Partial oxidation consists of sub-stoichiometric oxidation of hydrocarbons, while autothermal reforming integrates partial oxidation with steam reforming. Theoretically, both partial oxidation and autothermal reforming offer significant lower energy requirement and higher gas-space velocity than steam reforming reaction [9].

Focusing on fuel selection, among above hydrocarbon fuels, liquefied petroleum gas (LPG) is one of the good candidates for applying as a primary fuel for SOFC particularly in remote areas where pipeline natural gas is not available due to its easy transported and enable to store on-site [10,11]. In Japan, LPG and kerosene are promising alternative fuels for H_2 production along with natural gas due to their cost effective and easy distribution [12]. Typically, LPG is a mixture of C_3H_8 and C_4H_{10} (with various ratios depending on its source) that exist as liquids under modest pressures at ambient temperatures [13]. For instance, the composition of LPG from Australian LPG Association ranges from pure C_3H_8 to a 40:60 mixture of C_3H_8 and C_4H_{10} [14], whereas the composition of LPG from PTT Company (Thailand) is 60% C_3H_8 and 40% C_4H_{10} . Previously, most of studies over the reforming and relevant reactions of LPG have been carried out over noble metal catalysts (e.g. Rh, Ru, and Pt) on oxide supports [15–21]. The main products from the reforming of LPG are known to be H_2 , CO, and CO_2 ; nevertheless, the formations of C_2H_6 , C_2H_4 , and CH_4 are also generally observed due to the decomposition of LPG and methanation reactions. These formations particularly C_2H_6 and C_2H_4 are the major difficulty for converting of LPG to hydrogen-rich gas since these elements easily decomposes to carbon species at moderate temperature and eventually deposits on the surface of catalyst and/or anode material of SOFC, which considerably degrades the reactivity of catalyst and SOFC anode.

This work is aimed at the development of a catalyst for partial oxidation of LPG, which provides high stability and activity at such a high temperature (700–900 °C) for later application as an in-stack reforming of SOFC (IR-SOFC). Although Pt, Rh and Ru have been reported to provide high activity for the reforming and relevant reactions with excellent resistant to the carbon formation [22,23], the current prices of these metals are very high and the availability of some precious metals i.e. Ru was too low to have a major impact on the total reforming catalyst market [24]. In view of these economical considerations, an alternative catalyst was developed and studied instead. Ceria and doped ceria with Gd, Nb, La, and Sm have been reported as a catalyst in a wide variety of reactions involving oxidation or partial oxidation of hydrocarbons (e.g. automotive catalysis). A high oxygen mobility [25], high oxygen storage capacity [26], strong interaction with the supported metal (strong metal–support interaction) [27] and the modifiable ability [28] render these materials very interesting for catalysis. Importantly, ceria-based materials have been reported to have reactivity toward the decomposition of CH_4 at such a high temperature (800–1000 °C) with greater resistance toward carbon deposition compared to conventional metallic catalysts. The

addition of ZrO_2 to ceria, as Ce- ZrO_2 , has been reported to improve the oxygen storage capacity, redox property, thermal stability and catalytic activity of ceria [29–31]. This high oxygen storage capacity was associated with enhanced reducibility of cerium (IV) in Ce- ZrO_2 , which is a consequence of the high O^{2-} mobility inside the fluorite lattice. Due to the high thermal stability of this material, Ce- ZrO_2 would be a good candidate to be used as an in-stack reforming of SOFC.

In the present work, the reactivity toward the partial oxidation of LPG over Ce- ZrO_2 (at various Ce/Zr ratios), and doped Ce- ZrO_2 with Gd, Nb, La, and Sm was studied in order to determine the suitable material for this reaction and to investigate the benefit of these element (i.e. Gd, Nb, La, and Sm) doping; it is noted that the partial oxidation over Ni/ Al_2O_3 was also carried out for comparison. The influences of inlet O_2 /LPG molar ratio and temperature on the product compositions and the amount of carbon formation over these catalysts were determined. Lastly, an alternative concept to maximize the yield of H_2 production from LPG by applying sequential partial oxidation/steam reforming operation and using ceria-based material as primary oxidative catalyst was proposed and compared to the typical autothermal reforming over Rh/ Al_2O_3 ; detail of this study is explained in Section 3.5.

2. Experimental

2.1. Catalyst preparation and characterization

Ce- ZrO_2 was chosen as a based catalyst in the present work. This material with different Ce/Zr molar ratios was prepared by co-precipitation of $Ce(NO_3)_3$ and $Zr(NO_3)_4$ in the presence of 0.1 M cetyltrimethylammonium bromide solution (from Aldrich) as a cationic surfactant. We previously reported that the preparation of ceria-based materials by cationic surfactant-assisted method can provide materials with high surface area and good stability after thermal treatment [32]. The achievement of high surface area material from this preparation technique is due to the interaction of hydrous oxide with cationic surfactants under basic condition [33], while the high thermal stability are 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; this incorporation reduces the shrinkage and collapse of the catalyst during heating up, which consequently help the catalyst maintaining high surface area after calcinations [33].

The ratio between $Ce(NO_3)_3$ and $Zr(NO_3)_4$ was altered to achieve Ce/Zr molar ratios of 1/3, 1/1 and 3/1, while the molar ratio of ($[Ce]+[Zr]$)/[cetyltrimethylammonium bromide] was kept constant at 0.8. The solid solution was formed by the slow mixing of this metal salt solution with 0.4 M of urea. After preparation, 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 900 °C for 6 h. As for the synthesis of doped Ce- ZrO_2 with Gd, Nb, La, and Sm, these materials were prepared by mixing $Ce(NO_3)_3$ and $Zr(NO_3)_4$ with $RE(NO_3)_x$ ($RE = Gd, Nb, La, \text{ and } Sm$) to achieve the RE ratio in the material of 0.1; $RE_{0.1}$ -Ce ZrO_2 .

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