Applied Catalysis B: Environmental 144 (2014) 277–285

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Glycerol steam reforming over perovskite-derived nickel-based catalysts

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A R T I C L E I N F O

Article history:
Received 11 May 2013
Received in revised form 8 July 2013
Accepted 11 July 2013
Available online 19 July 2013

Keywords:
Hydrogen
Ni-based catalyst
Perovskite-type oxide
Glycerol steam reforming
Metal-support interaction

A B S T R A C T

This paper describes the synthesis and application of $La_{1-x}Ca_xNiO_3$ perovskite-type oxides in glycerol steam reforming. Various techniques including N_2 adsorption-desorption, X-ray diffraction, H_2 temperature-programmed reduction, temperature-programmed oxidation, H_2 chemisorption, transmission electron microscopy, and thermogravimetric analysis were used to characterize the prepared catalysts. The results showed that the perovskite structure could promote the even distribution of the containing elements (Ni, La or Ca) upon reduction, which led to the increase in the interfacial area between Ni and oxides *via* a confinement effect. Consequently, stronger metal-support interaction and smaller Ni metallic particles were observed on $LaNiO_3$, rather than Ni/La_2O_3 catalyst prepared by the impregnation method. Effects of lanthanum substitution by calcium on properties of the perovskite-type oxides were also studied. $La_{0.5}Ca_{0.5}NiO_3$ was the optimized composition for the steam reforming catalysts, owing to its strong metal-support interaction and high metal dispersion resulted from the synergetic interaction of La and Ca. Both properties were critical to the performance of glycerol steam reforming catalysts. Additionally, spent catalysts (e.g., upon 30 h stability test) were also characterized, which revealed the deactivation of catalysts was ascribed to coke deposition that covers the active sites. Specifically, smaller Ni particle size and stronger metal-support interaction could suppress carbon deposition, and thus improved the catalyst stability in glycerol steam reforming.

1. Introduction

With the diminishing reserves of fossil fuels, it is urgent to develop sustainable energy resources. Bio-diesel, derived from transesterification of vegetable oils, animal products, or waste fats, was proposed to be the substitute for diesel [1–3]. Nowadays, a large amount of crude glycerol, usually containing methanol, water and salts, are produced as the byproduct of bio-diesel (100 kg of glycerol per ton of bio-diesel) with the rapid growth of the bio-diesel industry [4–8]. To make bio-diesel economically competitive to regular diesel at the present stage, it is essential to develop technologies to improve the utilization of crude glycerol. However, the main and traditional applications of glycerol (food additives, health care and pharmaceuticals) are significantly restricted to low-quality glycerol unless an energy-intensive purification step is previously carried out [1,4,9]. Among those other markets for which crude glycerol may be directly utilized, the use of this resource as a source of hydrogen provides a possible solution for the dilemma, especially in the case of large-scale production [2,5,10,11].

Hydrogen is widely used in the chemical and petroleum industries, as well as identified as a promising clean energy for electrical power generation and fuel cell devices [12]. H_2 used in current industries is primarily produced from steam reforming of natural gas, during which a large amount of CO_2 was discharged [13]. However, it is deemed as a carbon-neutral process to utilize the renewable glycerol. Therefore, the production of hydrogen from renewable glycerol could contribute to the reduction of greenhouse gases and the sustainable development of modern economy [10,13–15].

$$C_3H_8O_3 + 3H_2O \leftrightarrow 7H_2 + 3CO_2 \quad \Delta H_{298\,K} = +128\,kJ/mol \qquad (1)$$

Various types of catalytic conversion systems such as pyrolysis, [16] partial oxidation and autothermal reforming [17,18], aqueous phase reforming [19,20], and steam reforming [21–24] have been investigated to convert glycerol to hydrogen and have been extensively discussed in previous work (see reviews [25–27]). Among these processes, glycerol steam reforming (GSR, Eq. (1)) is the most common one due to its ambient pressure reaction condition and high selectivity compared to aqueous phase reforming [28,29].

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http://dx.doi.org/10.1016/j.apcatb.2013.07.028

Though usually operated at relatively high temperatures (e.g., above 400 °C), this endothermic process could also be compensated by other exothermic ones (e.g., Fischer–Tropsch, methanol syntheses) to realize an available energy-efficient route for the H_2 production [10,14]. Nickel-based catalysts have been commercialized for industrial steam reforming processes including GSR in laboratory scale [27,30,31]. At present, carbon deposition and metal sintering are the major challenges for designing GSR catalysts [27]. As reported in previous work, nickel particle size and metal-support interaction (MSI) had significant effects on the performance of GSR catalysts [22,31,32], and our previous work also proved that these properties could be modified by the synthesis of a certain particular structure (e.g., hydrotalcite-like structure, phyllosilicate structure and inset of metal particle in the frame of the oxides) [33–35].

Recently, perovskite-type oxides have received increasing attention worldwide in steam reforming process due to its special crystal structure [36,37,21,38,39]. Perovskites are mixed oxides with a general formula of ABO_3, where A is an alkali, alkaline earth or rare earth metal and B is usually an element in the transition series [40,41]. Both A and B can be partially substituted with a great range of metal cations within the size constraints of the A and B sites, leading to a wide variety of compounds with modified catalytic, redox and structural properties [42]. These mixed oxides with well-defined cubic structure are capable of producing well-dispersed metallic particles upon reduction treatment [43–45]. Thus, the catalysts derived from perovskite-type oxides could avoid carbon formation, and present superior catalytic activity and stability [43,46]. Among these suitable perovskite-type oxides for reforming reaction, $LaNiO_3$ was widely studied due to its high catalytic activity [43,44,47,48]. Additionally, the effect of partial substitution of La by other metal (Ce, Ca, Sr, Sm, Nd, etc.) was also investigated in order to introduce the structural and electronic defects or enhance the interaction with B-site metal, which helped achieve highly active and stable catalysts [36,39,49,50].

Among these substitution elements, as a well-known alkaline earth metal, Ca has been used as a catalyst promoter in various kinds of reactions (e.g. methane dry reforming [51], ethanol steam reforming [52], oxidative steam reforming of glycerol [53]). The calcium dopant has been proved to generate positive catalytic effect in terms of higher activity and stability. However, the information about the performance of perovskite-type oxides, as well as the substitution of La by Ca, in GSR is limited [21]. Therefore, this paper describes a detailed investigation regarding the application of $La_{1-x}Ca_xNiO_3$ (x = 0.0, 0.1, 0.3, 0.5, 0.7 and 1.0) in GSR. Various techniques including N_2 adsorption-desorption, X-ray diffraction (XRD), H_2 temperature-programmed reduction (TPR), H_2 chemisorption, temperature-programmed oxidation (TPO), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA) were performed to characterize the prepared catalysts. The catalytic performance of the derived nickel-based catalysts in GSR was investigated and compared with a reference Ni/La_2O_3 catalyst.

2. Experimental

2.1. Catalyst preparation

The $La_{1-x}Ca_xNiO_3$ perovskite-type oxides used in this study were prepared by decomposition of amorphous citrate as described previously [36,54]. $Ni(NO_3)_2{\bullet}6H_2O$ (98.0%, Shanghai Chemical Reagent Company of National Medicine Group), $Ca(NO_3)_2{\bullet}4H_2O$ (98.0%, Shanghai Chemical Reagent Company of National Medicine Group) and $La(NO_3)_3{\bullet}6H_2O$ (98.0%, Tianjin Jierzheng Chemical Co., Ltd.) with desired molar ratios were dissolved in deionized water. Then, a concentrated solution of citric acid (98.0%, Tianjin No.1 Chemical Reagent Factory) with 20% excess over the total molars of cations was prepared and added to the nitrate solution. The resulting solution was heated to 60 °C and kept at this temperature for 9 h, followed by evaporating for 0.5 h using a vacuum rotary evaporator. The viscous solution was then dried at 120 °C for 12 h, which resulted in a spongy solid. The resultant solids were grinded and calcined in two stages: first at 300 °C for 2 h and then at 800 °C for 5 h, to obtain the final perovskite structure. Though not all the samples present perovskite structure, the nomenclature $La_{1-x}Ca_xNiO_3$ is used in all cases for uniformity and labeled as LCx (x = 0.0, 0.1, 0.3, 0.5, 0.7 and 1.0) [36].

A reference Ni/La_2O_3 catalyst containing the same Ni content as LC0.0 was also prepared by the impregnation method. The La_2O_3 support was first obtained by calcining the lanthanum nitrate at 800 °C, and then impregnated in a $Ni(NO_3)_2$ solution by mechanical agitation at 60 °C for 9 h, followed by evaporation at 60 °C using a vacuum rotary evaporation until the water was removed. The resultant solid was dried at 120 °C for 12 h, and then calcined at 800 °C for 5 h.

2.2. Physical characterization

XRD measurements were performed with 2θ values between 10 and 85° by using a Rigaku C/max-2500 diffractometer employing the graphite filtered Cu Kα radiation (λ = 1.5406 Å). The Scherrer equation was used to estimate the mean Ni crystallite size based on the diffraction peaks of the Ni (1 1 1) facet.

Textual properties of the catalysts were measured with a Micromeritics Tristar 3000 analyzer by nitrogen adsorption at −196 °C. The samples were degassed at 300 °C for 4 h prior to measurements. This instrument employed the Brunauer–Emmett–Teller (BET) method by measuring the quantity of nitrogen absorbed at −196 °C and the cumulative volumes of pores were obtained by the Barrett–Joyner–Halenda (BJH) method from the desorption branches of the adsorption isotherms.

H_2-TPR was employed to analyze the reduction behavior of the catalysts by using a Micromeritics AutoChem 2920 apparatus. A powered sample (50 mg) was pretreated at 700 °C for 1 h under flowing Ar (30 ml min^{-1}). Upon cooling to 50 °C, a flow rate of 30 ml min^{-1} of 10 vol% H_2/Ar was used for the reduction and the temperature was increased linearly from 50 to 800 °C at 10 °C min^{-1}.

TPO was carried out by using a Micromeritics AutoChem 2920 apparatus equipped with a HIDEN QIC-20 mass spectrometer (MS). The spent catalyst (20 mg) was pretreated at 800 °C for 1 h under flowing Ar (30 ml min^{-1}). Upon cooling to 100 °C, a flow rate of 30 ml min^{-1} of air was used for the oxidation and the temperature was increased linearly from 100 to 750 °C at 10 °C min^{-1}. The CO_2 in the effluent was monitored and recorded online by MS.

The quantitative content of Ni in prepared samples was measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) (VISTA-MPX, Virian). Prior to measurements, the samples were digested in HCl and HNO_3 aqueous solution assisted by microwave (Multiwave 3000, Anton Paar).

Dispersion of nickel was studied by employing H_2 chemisorption. For each run, 200 mg of catalyst were pre-reduced with 10 vol% H_2/Ar at 650 °C for 1 h, and then flushed with Ar at 650 °C for 30 min. H_2 chemisorption was carried out at 50 °C by injection pulses of 10 vol% H_2/Ar (0.5082 mL) every 4 min until the consumption peaks became stable (about 10 pulses).

TEM was conducted to characterize the morphology of catalysts employing a JEM-2100F transmission electron microscope at 200 kV. The microscope was also equipped with a liquid nitrogen cooled energy-dispersive X-ray spectroscopy (EDS) detector for elemental analysis. The sample was first dispersed in ethanol and