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Steam Reforming of Glycerol Over Nano Size Ni–Ce/LaAlO₃ Catalysts

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In this work, hydrogen production from glycerol by Steam Reforming (SR) was studied by Ni–Ce catalysts supported on LaAlO₃ perovskite in order to effect of the cerium loading amount and the reaction conditions. Nano size Ni–Ce/LaAlO₃ catalysts were prepared by precipitation method. The structure of the catalysts was characterized by XRD analysis. The morphology, dispersion and the reduction properties of catalysts was examined by SEM, TEM, H₂-chemisorption and TPR, respectively. It was found that 15 wt% Ni-5 wt% Ce/LaAlO₃ catalyst showed the highest glycerol conversion and hydrogen selectivity. In addition, the catalyst also showed the high carbon dioxide selectivity and the lowest methane selectivity. The results indicate that the catalyst promotes methane reforming reaction. The highest activity in the 15 wt% Ni–5 wt% Ce/LaAlO₃ was attributed to the proper cerium loading amount. Moreover, the lowest metal crystal size and rise in active site were found to have an effect on catalytic activity and hydrogen selectivity. The 15 wt% Ni–5 wt% Ce/LaAlO₃ catalyst exhibited excellent performance with respect to hydrogen production at reaction temperature of 450 °C, at atmospheric pressure, 20 wt% glycerol solution and GHSV = 6,000 mL/ g-cat hr.

Keywords: Glycerol, Hydrogen Production, Nickel, Cerium, Steam Reforming.

1. INTRODUCTION

Recently, extensive use of fossil fuels has led to emergence problems: like depletion of petroleum reserves, global warming, acid rain, etc. Consequently, the renewable and environmental resource, Bio-diesel has attracted considerable interest worldwide.¹ Bio-diesel can be produced by the trans-esterification reaction of triglyceride with methanol; by-product 10 wt% glycerol. It is proposed that an increase in the production of Bio-diesel from renewable raw materials will result in an overabundance of glycerol in the market, which can possibly be supplied at low cost. Many investigators have focused on steam reforming of glycerol as a hydrogen production process. The hydrogen is considered as the future clean energy vector, thus gaining more importance with the subsequent development of fuel cells and the rising energy demands.²

Steam reforming of glycerol theoretically generates only carbon dioxide and hydrogen, according to reaction Eq. (1).

$$C_3H_8O_3 + 3H_2O \leftrightarrow 3CO_2 + 7H_2 \tag{1}$$

Reaction in Eq. (1) may be viewed as the combination of the glycerol decomposition (Eq. (2)) and water-gas-shift reaction (Eq. (3)).

$$C_3H_8O_3 \leftrightarrow 3CO + 4H_2$$
 (2)

$$CO + H_2O \leftrightarrow CO_2 + H_2$$
 (3)

The noble metals (Rh, Pt) were found to have promising catalytic performance in terms of conversion and selectivity for steam reforming of glycerol.³ However, high cost

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and low availability of these metals have led to a search for alternative metals, which are cheaper and more readily available. For that reason, nickel based catalysts are widely used due to their high activity at much lower cost.

However, the main problem encountered was the formation of carbon deposits and deactivation by of the catalyst due to Ni sintering. It is hence highly desirable to develop catalyst that is inexpensive, active and stable during the glycerol reforming reaction. According to the literature, Ce and La have been described to inhibit the growth of metal particles and favor the removal of carbon deposits from metal surface.⁴

The aim of the present work was to investigate the hydrogen production in steam reforming of glycerol over Ni based catalysts. The Ni–Ce and Ni–La catalysts supported on LaAlO₃ perovskite employed Ce and La loading amount 5 wt%, respectively. Catalyst of Ni supported on LaAlO₃ perovskite was also prepared for a comparative analysis. The physicochemical properties of both the catalysts were characterized and correlated with their catalytic performance.

2. EXPERIMENTAL DETAILS

2.1. Catalyst Preparation

The used perovskite was in the form of ABO₃, with La in the A sites and Al in the B sites. This LaAlO₃ perovskite was prepared by means of the citric acid-method, in which citric acid was added to the sol-gel method.⁵ The mixture was obtained in the form of a gel, dried at 110 °C overnight in an oven and calcined at 400 °C for 2 h and 850 °C for 11 h in air.

The catalysts of $15Ni/LaAlO_3$, $15Ni-5Ce/La-AlO_3$ and $15Ni-5La/LaAlO_3$ were prepared by means of a precipitation method using Na_2CO_3 , in which the Ni loading amount was 15 wt% and the Ce, La loading amounts were 5 wt%, respectively.

The precipitate was stirred at 80 °C for 1 h, then repeatedly washed and filtered with distilled water and finally dried overnight at 110 °C in oven. Subsequently, all the synthesized catalysts were calcined at 500 °C for 5 h.

2.2. Catalysts Characterization and Reaction Test

Catalysts were characterized by X-ray diffraction (XRD) instrument (Rigaku, Japan, DMAX100, Cu-K α , Ni filter), Scanning electron microscope (SEM) instrument (JEOL, JSM-5400A), Transmission electron microscope (TEM) instrument (JEOL, JEN-2000FXII), H₂-chemisorption and Temperature-programmed reduction (TPR) instrument (Chemisorption Analyzer, BEL-CAT, BEL, Japan).

The steam reforming of glycerol was carried out under atmospheric pressure in a fixed-bed reactor. Prior to the reaction, the catalyst was reduced *in situ* at 550 °C for 2 h in a mixture of H₂ (3 ml/min) and Ar (27 ml/min). The reactor consisted of a stainless steel (i.d. = 16 mm), (L = 400 mm) tubular reactor to hold the catalyst and it was located inside an electric oven of low thermal inertia. The temperature inside the reactor is measured by means of a thermocouple, located inside the catalytic bed. Typically, 1 g of catalyst was loaded in the reactor and an aqueous solution containing glycerol was fed into the reactor by an HPLC (high-pressure liquid chromatography) pump. The product stream was separated into a liquid phase and a gas phase in a condenser connected to the reactor outlet. The gaseous products were analyzed on-line by gas chromatography using a Shimatzu-14B model chromatograph equipped with a TCD (thermal conductivity detector). Finally H₂, CH₄, CO and CO₂ were separated in a Hayesep D column ($\Phi 1/8'' \times 7$ m, 100/120 mesh) using Ar as the carrier gas.

3. RESULTS AND DISCUSSION

3.1. Characterization of Catalysts

The XRD measurements of prepared LaAlO₃ supported Ni catalyst and Cerium, Lanthanum promoted Ni/LaAlO₃ catalysts are shown in Figures 1(A) and (B), respectively. All the catalysts exhibit strong diffraction peaks that appear around $2\theta^{\circ} = 33^{\circ}$, corresponding to perovskite structures.

For the calcined catalysts (Fig. 1(A)), the diffraction lines of nickel phases were presented at $2\theta^{\circ} = 37.2^{\circ}$, 43.4° and 63° for NiO in all catalysts.⁶ Figure 1(B) shows the 550 °C for 2 hours. The diffraction lines show that NiO logy to: McMaster University



Figure 1. XRD patterns of calcined catalysts (A) and reduced catalysts (B): (a) Ni/LaAlO₃, (b) Ni–Ce/LaAlO₃, (c) Ni–La/LaAlO₃.

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Table I. Physicochemical properties of different catalysts.					
Catalyst	Ni size (nm) ^a	Metal dispersion (%)			
Ni/LaAlO ₃	33	2.3			
Ni-Ce/LaAlO ₃	26	3.2			
Ni–La/LaAlO ₃	31	1.3			

Notes: a Sized of Ni particles on catalysts determined by Scherrer equation.

was completely reduced to Ni, at $2\theta^{\circ} = 44.5^{\circ}$ and 51.8° . The crystallite sizes of Ni in the catalysts were determined using Scherrer equation. It was evident that the Ni/LaAlO₃ catalyst has relatively large Ni crystallites (33 nm), while they were significantly smaller in modified catalysts.

Table I shows the physicochemical properties of Ni catalysts. Ni Size of Ni/LaAlO₃, Ni-Ce/LaAlO₃ and Ni-La/LaAlO₂ was measured as 33, 26 and 31 nm, respectively. The Ni-Ce/LaAlO₃ catalyst exhibited smallest Ni size; this result was in agreement with the conclusion revealed by SEM micrograph (Fig. 2).7 Also, Table I shows the metal dispersion of catalysts measured using H₂-chemisorption. Metal dispersion was found to be 2.3, 3.2 and 1.3% for Ni/LaAlO₃, Ni-Ce/LaAlO₃ and Ni-La/LaAlO₃, respectively. Therefore, we concluded that more active sites were present on the Ni-Ce/LaAlO3 catalyst surface than on the other catalysts. Figure 2 shows the SEM images of the calcined and used catalysts. In all the SEM images of catalysts, the metal was observed to be supported on the perovskite support and the metal particles were dispersed into sized particles. Figure 3 shows the TEM images of the calcined and used catalysts. After reaction, Ni/LaAlO₃ catalyst exhibited two kinds of carbon deposits whisker-type and encapsulating carbon. However, Ni-Ce/LaAlO₃ catalysts had deposits of whisker-type carbons. According to the literature, whiskerlike carbon possess essentially no or little toxicity, but encapsulating carbon deposits have high toxicity, which could progressively encapsulate the Ni particles, thus hindering the access of the reacting gasses to the active surface.⁸

The TPR profiles of catalysts are shown in Figure 4 the Ni/LaAlO₃ catalyst presented a reduction peak at low temperature (345 °C), which can be attributed to the reduction of NiO species on the surface of the support. The reduction peaks of Ni-Ce/LaAlO₃ and Ni-La/LaAlO₃ catalysts are evident at 360 and 385 °C,9,10 respectively. An evident shift in the reduction peaks of Ni species to high temperature can be seen in the profile, suggesting that the introduction of Ce can improve the interaction between Ni species and catalyst environment.⁷ The catalysts promoted with Ceri um exhibited less reducible activity than the Ni/LaAlO3 catalyst attributable to the increase in the metal-support interaction and better nickel dispersion. Consequently, it can be concluded that Ce species obviously reduces the size of Ni particles and improves the interaction between the Ni species and environment.

3.2. Catalytic Activity

Table II summarizes the extent of glycerol conversion and product selectivity of glycerol steam reforming on Ni/LaAlO₃, Ni–Ce/LaAlO₃ and Ni–LaAlO₃ catalysts at conditions of 20 wt% glycerol solution, 450 °C reaction temperature and GHSV = 6,000 mL/g-cat \cdot ht. When compared to the Ni/LaAlO₃ catalyst, both La and Ce modified Ni/LaAlO₃ catalysts achieved higher glycerol conversion. Regarding gas products distribution, lower methane selectivity was observed for La, Ce modified Ni/LaAlO₃ catalysts. This observation is indicative of higher activity in the methane steam reforming.

The Ni–Ce/LaAlO₃ catalyst demonstrated the highest conversion of glycerol and H_2 selectivity than other catalysts. Furthermore, because of smaller Ni particle size, the catalyst exhibited good catalytic performance. It is also indicative from the study that Ni particle size and



Figure 2. SEM images of Ni/LaAlO₃, Ni–Ce/LaAlO₃ and Ni–La/LaAlO₃ catalysts. (1) Ni/LaAlO₃ (a) before and (a') after reaction, (2) Ni–Ce/LaAlO₃ (b) before and (b') after reaction, (3) Ni–La/LaAlO₃ (c) before and (c') after reaction.



Figure 3. TEM images of Ni/LaAlO₃, Ni–Ce/LaAlO₃ and Ni–La/LaAlO₃ catalysts. (1) Ni/LaAlO₃ (a) before and (a') after reaction, (2) Ni–Ce/LaAlO₃ (b) before and (b') after reaction, (3) Ni–La/LaAlO₃ (c) before and (c') after reaction.



Figure 4. TPR analysis of catalysts : (a) Ni/LaAlO₃, (b)Ni-Ce/LaAlO₃, (c) Ni–La/LaAlO₃ catalysts.

Metal dispersion had an effect on the catalytic performance of the catalyst. The Ni–Ce/LaAlO₃ catalyst exhibited high carbon dioxide selectivity and lower carbon monoxide and methane selectivity. This indicates that the catalyst favored water–gas shift reaction (CO + $H_2O \leftrightarrow CO_2 + H_2$) and methane steam reforming reaction (CH₄ + H₂O \leftrightarrow CO + 3H₂).

Table II. Glycerol conversion and gas product selectivity in the presence of different catalysts (20 wt% glycerol, 450 °C, $GHSV = 6,000 \text{ mL/g-cat} \cdot \text{hr}$).

Catalysts	Conversion (%)	H ₂ Selectivity (%)	C ₁ compound selectivity (%)		
			СО	CH_4	CO_2
Ni/LaAlO ₃	87.8	60.8	0.2	7.4	92.4
Ni-Ce/LaAlO ₃	94.6	63.4	0.5	2.9	96.6
Ni-La/LaAlO ₃	89.2	61.1	0.4	2.2	97.4

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4. CONCLUSION

The performance of Ni/LaAlO₃ catalysts promoted with Ce, La for glycerol steam reforming was investigated. The Ce modified nickel perovskite catalyzed the formation of small Ni particle size as confirmed by XRD and SEM analyses. The Ni-Ce/LaAlO₃ catalyst for the glycerol steam reforming at 450 °C exhibited the best result. In addition, the Ni-Ce/LaAlO3 catalyst led to higher water-Mon gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) and methane an Ssteam reforming reaction $(CH_4 + H_2O \leftrightarrow CO + 3H_2)$. Furthermore, the consequence of interaction between the Ni particles and support might well-explain the beneficial influence of the catalytic activity for glycerol reforming reactions. Thus, it is concluded that Ni particle size and the metal dispersion served as important factors in determining the catalytic activity for hydrogen production by steam reforming of glycerol.

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