[Article]

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铈镧比对 $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ 系催化剂甘油氧化蒸汽重整制氢性能的影响

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摘要: 利用共沉淀法制备了 CeO_2 和 La_2O_3 复合载体的 $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ (CeNiLaO) 系催化剂, 在固定床反应器中考察其甘油氧化蒸汽重整制氢(OSRG)性能, 并采用X射线衍射(XRD)、程序升温还原(H_2 -TPR)、激光拉曼光谱(Raman)、扫描电子显微镜(SEM)、透射电子显微镜(TEM)和X射线光电子能谱(XPS)等手段对催化剂进行表征分析。结果表明: La_2O_3 能够有效地分散Ni颗粒, 减弱Ni颗粒在反应过程中的烧结, CeO_2 提供的晶格氧能够消除催化剂表面的积碳, 同时La会部分进入Ce的晶格取代部分 Ce^{4+} 造成晶格畸变, 提高表面的氧空穴数。 La_2O_3 和 CeO_2 的共同作用有利于减弱Ni因为烧结和积碳引起的失活。在不同Ce/La摩尔比的催化剂中, $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ 表现出最好的催化活性, 并且该催化剂在长达210 h的稳定性测试中, 甘油的转化率都在95%以上, 气相产物中的氢气浓度达50%。

关键词: 氧化铈; 氧化镧; 镍; 稳定性; 甘油; 制氢; 蒸汽重整

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$\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ Catalysts for Hydrogen Production by Oxidative Steam Reforming of Glycerol: Influence of the Ce-to-La Ratio

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Abstract: $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ (CeNiLaO) catalysts were synthesized using a Ce-La composite oxide as the carrier via co-precipitation. They were applied in the oxidative steam reforming of glycerol (OSRG) in a fixed-bed reactor. The catalysts were characterized by X-ray diffraction (XRD), H_2 -temperature-programmed reduction (H_2 -TPR), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The results showed that La_2O_3 improved the dispersion of metallic Ni and suppressed the sintering of metallic Ni particles; the lattice oxygen of CeO_2 inhibited and eliminated carbon deposition on the surface of the catalysts; and the substitution of some La^{3+} for Ce^{4+} ions induced a distortion of the lattice. The synergy of La_2O_3 and CeO_2 lessened the deactivation caused by the sintering and coke deposition and improved the catalytic performance. Among the catalysts with different molar ratios of Ce to La, $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ had the best catalytic activity. The conversion of glycerol remained above 95% after a 210 h stability test, while a gaseous reformat of about 50% hydrogen could be steadily produced.

Key Words: CeO_2 ; La_2O_3 ; Ni; Stability; Glycerol; Hydrogen production; Steam reforming

1 Introduction

Hydrogen has been widely applied in fine chemicals and pe-

troleum industries as a chemical raw material. Meanwhile, hydrogen is also considered as a potential clean and environmental

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friendly energy carrier, with high calorific value and zero pollution. At present, hydrogen is produced mainly by the steam reforming of natural gas in chemical industry. However, this process suffers from the unsustainable raw material and substantial carbon dioxide emissions. Renewable sources, especially those from biomass, are ideal feedstock to produce hydrogen, which makes this process sustainable and recycle CO₂ back to grow more biomass¹.

Glycerol is the major by-product from the transesterification of fatty acids to manufacture biodiesel, providing about 10% as glycerol. With the rapid growth of biodiesel production, glycerol has been increasingly produced in recent years. Thus, the application of glycerol has constrained the development of biodiesel industry². Conversion of glycerol to hydrogen is one of the most attractive ways to make use of glycerol, which can either alleviate the oversupply of glycerol, or afford a renewable hydrogen production independent on fossil fuels.

Hydrogen can be produced from glycerol by the steam reforming (SRG) reaction with catalysts. Noble metal catalysts, such as Pt, Ru, Rh, and Ir³⁻⁵, have been proved to be highly active for the SRG reaction, but are limited by the cost and resources. Compared with noble metal, Ni has attracted intensive research interests as a representative base metal catalyst⁶⁻⁹. Wu *et al.*⁶ fabricated the supported Ni/Al₂O₃ catalyst with different Ni precursors. Under the optimum conditions, the yield of H₂ was about 5.5 mol · mol⁻¹ glycerol, approaching to the thermodynamic equilibrium value, 5.7 mol · mol⁻¹. Wang *et al.*⁸ developed a Ni-Mg-Al catalyst, which showed an optimal performance with the conversion of glycerol up to 88.0% and the yield of H₂ up to 78.5% at 650 °C. However, Ni-based catalysts generally suffer from the rapid deactivation caused by sintering and coke deposition during the SRG reaction process^{10,11}, which remains a major challenge for developing stable Ni-based catalysts.

It has been widely documented that an appropriate support is very important for the stability of Ni-based catalysts, because the supports may affect the metal dispersion and inhibit particle sintering and carbon formation¹²⁻¹⁵. Various oxides, including La₂O₃, Al₂O₃, CeO₂, ZrO₂, SiO₂, and MgO, have been investigated as supports of nickel^{6,12,15,16}. CeO₂ has excellent oxygen storage-release capability by readily altering its oxidation states between Ce⁴⁺ and Ce³⁺¹⁷. This property can be used to remove coke deposition on the metal surface and suppress deactivation. Gong *et al.*¹⁸ studied the effect of CeO₂ on the performance of steam reforming of ethanol (SRE) over ceria-promoted Ni/SBA-15 catalysts and found that ceria promoter suppressed the coke formation on catalyst surfaces. Liu *et al.*¹⁹ also found that at temperatures above 327 °C, the lattice oxygen from ceria could eliminate the coke formed in the process of SRE. Our previous works^{3,11} show that La₂O₃ is beneficial for the redispersion of active metals, thereby slows the deactivation caused by sintering. Moreover, La₂O₃ has a strong interaction with nickel at high temperatures through forming La-Ni-O phases, which stabilize the nickel^{20,21}. The incorporation of La₂O₃ could increase the dispersion of metallic Ni on Ni/γ-Al₂O₃ and restrain the sintering of Ni particles, thus improve the stability of Ni/γ-Al₂O₃ catalysts²². Both

CeO₂ and La₂O₃ could improve the stability of Ni-based catalysts as supports. Ce and La composite oxide may further enhance the stability as a catalyst carrier^{20,23}. Venezia *et al.*²⁰ compared the catalytic behavior of Ni catalysts supported over CeO₂, La₂O₃, and CeO₂-La₂O₃ mixed oxide in the methane partial oxidation reaction. It was found that in the presence of mixed CeO₂-La₂O₃ there was no coke formed. Arias *et al.*²³ also found that, when CeO₂ and La₂O₃ co-existed simultaneously, the catalysts displayed excellent stability. In this work, we synthesized Ce_xNi_{0.5}La_{0.5-x}O catalysts utilizing Ce and La composite oxide as a carrier *via* co-precipitation method and optimized the ratio of CeO₂ to La₂O₃, to enhance the stability of Ni-based catalysts for the oxidative steam reforming of glycerol (OSRG) reaction.

2 Experimental

2.1 Preparation of catalysts

All the reagents are analytic pure and were purchased from Sinopharm Chemical Reagent Co., Ltd. Catalysts in this paper were synthesized *via* a co-precipitation method. Typically, Ce(NO₃)₃ · 6H₂O, Ni(NO₃)₂ · 6H₂O and La(NO₃)₃ · nH₂O were dissolved in deionized water with desired Ce²⁺/La³⁺ molar ratios and a Ni content of 50% (atomic fraction) in final products, then the pH of the solution was adjusted to 11 by adding triethylamine solution dropwise. After continuously stirring for 4 h, the resulting white suspension was aged at room temperature for 2 h. The precipitates were filtered and washed with deionized water, followed by drying at 110 °C for 12 h, and then calcined in air at 650 °C for 6 h to obtain the catalysts. The samples were denoted as Ce_xNi_{0.5}La_{0.5-x}O, where *x* represents the molar fraction of Ce.

2.2 Characterizations

Specific surface areas of catalysts were measured by N₂ adsorption at -196 °C (ASAP 2010, Micromeritics, America). Before the measurements, the samples were degassed at 300 °C under vacuum overnight. Electron probe microanalysis (EPMA-1600, Shimadzu, Japan) was used to analyze the compositions of catalysts. Powder X-ray diffraction (XRD) measurements were performed in a Rigaku D/max-IIIAX diffractometer (Rigaku, Japan) using Cu K_α radiation (operating at 40 kV and 40 mA). H₂ temperature-programmed reduction (H₂-TPR) was employed to analyze the reduction behavior of the catalysts in a TP5080 adsorption instrument (Xian Quan, China) equipped with a thermal conductivity detector (TCD). The hydrogen consumption was measured by calculating the reduction peaks in the range of 100–500 °C referenced to the reduction peak of CuO as a standard material. X-ray photoelectron spectroscopy (XPS) was performed in a Kratos Axis ultra (DLD) spectrometer (Kratos, England) equipped with an Al K_α X-ray source. The binding energies were referenced to the C 1s peak at 284.8 eV. Raman spectra were recorded on a LabRAM Aramis micro Raman spectrometer (Renishaw, England) with 633 nm wavelength laser and 2 μm spot size. Transmission electron microscopy (TEM) measurements were performed in a TECNAI10 microscope (Philips-FEI, Holland) equipped with an INCA energy dispersive spectrometer operated

at 200 kV. Specimens for TEM were prepared by ultrasonically suspending the sample in acetone and depositing a drop of the suspension onto a copper grid covered by amorphous carbon. SEM was performed in a LEO-1530VP microscope (LEO, German).

2.3 Catalytic tests

The OSRG reaction was carried out in a quartz tubular reactor with inner diameter of 8 mm and length of 280 mm to evaluate the catalytic activity of the catalysts. The configuration and operation of reactor had been described in our previous work²⁴. Before reaction, 0.2 g catalyst was activated with H_2 at a flow rate of $30 \text{ mL} \cdot \text{min}^{-1}$ at 500°C for 20 min, then heated the reactor to the desired temperature under N_2 atmosphere. The gaseous products were analyzed by a gas chromatograph (He as carrier gas) equipped with a TCD and a flame ionization detector (FID). A TDX 01 column was used for H_2 , CO and CO_2 analysis in TCD. CH_4 and C_2H_4 were analyzed by FID with a packed column for analyzing transformer oil.

The glycerol conversion (C_{gly}) was calculated by

$$C_{\text{gly}} = \frac{\text{moles of carbon in gas products}}{3 \times F_{\text{in}}} \times 100\%$$

where F_{in} represent moles of glycerol fed.

The selectivity of H_2 was calculated by

$$S_{\text{H}_2} = \frac{\text{moles of } \text{H}_2 \text{ produced}}{\text{moles of carbon in gas products}} \times \frac{3}{4} \times 100\%$$

The selectivities of carbon containing species (CO , CO_2 , CH_4 , and C_2H_4) in gas products were calculated by

$$S_i = \frac{n \times \text{moles of } i}{\text{moles of carbon in gas products}} \times 100\%$$

where n is the atom number of carbon in i species.

3 Results and discussion

3.1 Catalyst characterizations

XRD patterns of fresh, reduced, and used catalysts with different Ce/La ratios are presented in Fig.1. CeO_2 , NiO , $\text{La}(\text{OH})_3$ and some characteristic peaks from LaNiO_3 were detected in the fresh catalysts. As the content of La increases, the characteristic peaks of CeO_2 shift to low-angle region (see inset of Fig.1(a)). Meanwhile, there are no peaks from La species at lower La contents, indicating that some La ions may enter into the lattice of CeO_2 and induce a lattice distortion. In addition, the peaks of NiO gradually broaden with the introduction of La, proving that La_2O_3 could increase the dispersion of NiO particles. The appearance of $\text{La}(\text{OH})_3$ may be resulted from the reaction between La species and moisture. After H_2 reduction at 500°C , NiO turns into Ni completely (Fig.1(b)). $\text{La}(\text{OH})_3$ would turn into $\text{La}_2\text{O}_3\text{CO}_3$ after the OSRG reaction (Fig.1(c)), probably through the decomposition of $\text{La}(\text{OH})_3$ to La_2O_3 and the carbonization of La_2O_3 to $\text{La}_2\text{O}_3\text{CO}_3$ ^{3,24}.

Table 1 summarizes the textual properties and crystallite sizes of fresh, reduced, and used catalysts with different Ce/La molar ratios. The Scherrer equation was used to estimate the mean crystallite size from the (111) diffraction peak of Ni or the (012) peak of NiO . The crystallite sizes of NiO and Ni decreased greatly after incorporating La, indicating the dispersion effect of La_2O_3 on nickel. The smallest Ni crystallite size is reached over the

Fig.1 XRD patterns of (a) fresh, (b) reduced, and (c) used $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ catalysts

Inset shows the characteristic peaks of CeO_2 shifting to low-angle region.

$\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ catalyst. In addition, the $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ also shows the highest specific surface area and pore volume. For all the catalysts, the sintering of Ni can be observed after the OSRG reaction, indicated by the increasing size of Ni particles. Nevertheless, the sintering of Ni particles would be somewhat retarded over the La-containing samples, indicated by the less increase of Ni particle size after the OSRG reaction, suggesting the improved thermal stability of catalyst²².

The TPR curves of $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ catalysts are shown in Fig.2. The weak reduction peak below 300°C could be ascribed to the reduction of highly dispersed Ni species on surfaces²⁵. The two overlapping peaks in the range of $300\text{--}500^\circ\text{C}$ could be assigned as the reduction of Ni^{2+} which has weak and strong interaction with support, respectively. The high temperature reduction peak of $\text{Ce}_{0.5}\text{Ni}_{0.5}\text{O}$ at 800°C is from the reduction of Ce^{4+} to Ce^{3+} ^{26,27}, which is absent for other catalysts, probably due to the stronger

Table 1 Compositions and physical properties of the fresh, reduced, and used $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ catalysts

Catalyst	Composition ^a /%				Size/nm			Specific surface area/($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume/($\text{cm}^3 \cdot \text{g}^{-1}$)
	Ce	Ni	La	O	fresh (NiO^b)	reduced (Ni^b)	OSRG used (Ni^b)		
$\text{Ce}_{0.5}\text{Ni}_{0.5}\text{O}$	25.09	25.71	0.00	49.20	24.2	20.7	42.4	30.7	0.113
$\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$	19.40	25.69	4.55	50.36	13.2	12.9	35.4	42.8	0.160
$\text{Ce}_{0.3}\text{Ni}_{0.5}\text{La}_{0.2}\text{O}$	15.34	30.31	8.20	46.15	12.3	13.9	34.0	21.3	0.121
$\text{Ce}_{0.2}\text{Ni}_{0.5}\text{La}_{0.3}\text{O}$	10.30	27.53	14.84	47.33	9.2	13.0	32.7	10.7	0.079
$\text{Ce}_{0.1}\text{Ni}_{0.5}\text{La}_{0.4}\text{O}$	4.72	25.57	20.32	49.39	7.4	14.6	25.7	16.0	0.115
$\text{Ni}_{0.5}\text{La}_{0.5}\text{O}$	0.00	23.09	23.26	53.66	14.1	15.2	25.6	13.4	0.058

reaction conditions: $T = 650\text{ }^\circ\text{C}$, carbon-to-oxygen molar ratio = 1, steam-to-carbon molar ratio = 4, gas hourly space velocity (GHSV) = 120000 h^{-1} , $t = 5\text{ h}$.

^aatomic fraction, measured by EPMA with fresh catalysts. ^bcrystallite sizes calculated by Scherrer equation.

metal-support interaction (MSI) over the mixed oxides. The strongest MSI is achieved on the composition of $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$, evidenced by the highest reduction peak temperature. Considering the refractory nature of La, the minor peaks of $\text{Ni}_{0.5}\text{La}_{0.5}\text{O}$ in the range from 500 to 650 $^\circ\text{C}$ can be attributed to the decomposition of $\text{La}_2\text{O}_3\text{CO}_3$ ³. The H_2 consumptions were calculated by integrating the peaks from room temperature (r.t.) to 500 $^\circ\text{C}$. Assuming Ni^{2+}

Fig.2 H_2 -TPR profiles of $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ catalysts

as the reducible species, the H_2 consumptions are very close to the theoretical values of $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ (from 90.8 to 94.3 $\text{mL} \cdot \text{g}^{-1}$).

As shown in Fig.3, the fresh $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ catalysts display similar porous structures composed of aggregated particles. H_2 -reduction has little effect on the catalyst morphology. Ni crystallites can be observed in TEM images (Fig.4). Compared with $\text{Ce}_{0.5}\text{Ni}_{0.5}\text{O}$, the $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ is comprised of smaller particles, being consistent with the results of XRD. It should be noticed that the lattice spacing of the (200) planes of CeO_2 in the $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ is 0.284 nm (inset of Fig.4(b)), which is larger than pure CeO_2 (0.2706 nm, PDF#43-1002), indicating the substitution of La for Ce ions as revealed by XRD results. The formation of Ce-La-O mixed oxides is also supported by the absence of any La species in the HR-TEM observation.

Fig.5 shows the Raman spectra of $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ catalysts and pure CeO_2 . Because of the intense fluorescent effect of La species on Raman spectra, the measurements were conducted for the samples with $x < 0.3$ to avoid the excessive amounts of La. The band at 464 cm^{-1} could be ascribed to the F_{2g} vibration mode of fluorite structure of CeO_2 ²⁸. When the amount of La increased, the band shifted to lower wave numbers, which may be caused by the

Fig.3 SEM images of fresh (a) and reduced (b) $\text{Ce}_{0.5}\text{Ni}_{0.5}\text{O}$, fresh (c) and reduced (d) $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ catalysts

Fig.4 TEM images of reduced (a) $\text{Ce}_{0.5}\text{Ni}_{0.5}\text{O}$ and (b) $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ and HR-TEM images of used $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ after OSRG reaction
reaction conditions: $T = 650^\circ\text{C}$, carbon-to-oxygen molar ratio = 1, steam-to-carbon molar ratio = 4, GHSV = 60000 h^{-1} , $t = 210\text{ h}$

Fig.5 Raman spectra of pure CeO_2 and $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ catalysts

incorporation of heteroatom ions into the lattice of CeO_2 ²⁹. Herein, we conclude that the shift probably stems from the incorporation of La or Ni as revealed by aforementioned analysis. Two overlapping bands in the range of $500\text{--}650\text{ cm}^{-1}$ can be observed for all the $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ catalysts. The band at 545 cm^{-1} could be attributed to the O^{2-} vacancy on catalyst surfaces, and the one at 615 cm^{-1} could be ascribed to the vacancy-interstitial oxygen defects in ceria³⁰. As shown in Fig.5, either La or Ni would create oxygen vacancies on catalyst surfaces, and the strong intensity of the defect-related bands of $\text{Ce}_{0.3}\text{Ni}_{0.5}\text{La}_{0.2}\text{O}$ suggests that the amount of oxygen vacancies could be tuned by catalyst composition.

Fig.6 reports the XPS spectra of $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ in the O 1s binding energy (BE) regions. The XPS spectra exhibit similar broad doublet peaks in all catalysts. The lower BEs can be assigned to lattice oxygen (labeled as OI) and the BEs with higher

Fig.6 O 1s XPS spectra of fresh $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ catalysts

values are attributed to other surface oxygen species (labeled as OII)^{31–33}. The surface oxygens (OII) increase with the incorporation of La³⁴ because of the formation of $\text{La}(\text{OH})_3$ or $\text{La}_2\text{O}_2\text{CO}_3$, as revealed by XRD, but, the amount of lattice oxygen changes in a contrary tendency. The results indicate La would increase the amount of OII and Ce could improve OI. Meanwhile, the shift of BE of OI toward lower values with incorporating La³⁺, see the cases $x = 0.1, 0.2, 0.3$, indicates that La ions have entered into the lattice of CeO_2 ³², which is agreement with the analysis of XRD, HR-TEM, and Raman spectroscopy.

3.2 Catalytic performance of $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ catalysts

OSRG and SRG reactions were performed under the optimized conditions established in our previous work³. Table 2 compares their catalytic performances. In SRG, $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ showed the best activity, indicated by the highest conversion of glycerol and

Table 2 Catalytic performance of $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ catalysts in SRG and oxidative SRG (OSRG)

Catalyst	OSRG ^a						SRG ^b					
	$C_{\text{gly}}/\%$	$S_{\text{CO}}/\%$	$S_{\text{CO}_2}/\%$	$S_{\text{CH}_4}/\%$	$S_{\text{C}_2\text{H}_6}/\%$	$\text{STY}_{\text{H}_2}/(\text{L}\cdot\text{g}^{-1}\cdot\text{h}^{-1})$	$C_{\text{gly}}/\%$	$S_{\text{CO}}/\%$	$S_{\text{CO}_2}/\%$	$S_{\text{CH}_4}/\%$	$S_{\text{C}_2\text{H}_6}/\%$	$\text{STY}_{\text{H}_2}/(\text{L}\cdot\text{g}^{-1}\cdot\text{h}^{-1})$
$\text{Ce}_{0.5}\text{Ni}_{0.5}\text{O}$	99.8	21.0	78.7	0.37	—	12.3	84.3	35.3	55.5	4.1	5.08	18.4
$\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$	100	24.7	75.1	0.24	—	13.4	98.9	32.2	60.3	6.8	0.68	21.6
$\text{Ce}_{0.3}\text{Ni}_{0.5}\text{La}_{0.2}\text{O}$	99.5	20.9	78.6	0.50	—	12.4	87.8	34.0	59.3	4.6	2.07	19.4
$\text{Ce}_{0.2}\text{Ni}_{0.5}\text{La}_{0.3}\text{O}$	97.7	23.2	75.5	1.38	—	12.7	55.7	38.4	43.5	2.7	15.31	9.5
$\text{Ce}_{0.1}\text{Ni}_{0.5}\text{La}_{0.4}\text{O}$	97.6	25.0	73.8	1.18	—	10.2	40.0	40.0	35.3	2.9	21.80	5.3
$\text{Ni}_{0.5}\text{La}_{0.5}\text{O}$	94.8	24.9	74.1	1.08	—	9.5	58.9	36.0	45.7	3.1	15.26	9.6

^areaction conditions: $T = 650^\circ\text{C}$, steam-to-carbon molar ratio = 2, carbon-to-oxygen molar ratio = 1, GHSV = 120000 h^{-1} , $t = 5\text{ h}$; ^breaction conditions: $T = 650^\circ\text{C}$, steam-to-carbon molar ratio = 2, GHSV = 120000 h^{-1} , $t = 5\text{ h}$; ^cspace time yield (STY) of H_2

Fig.7 Stability test of $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ in the OSRG reaction

reaction conditions: $T = 650\text{ }^{\circ}\text{C}$, carbon-to-oxygen molar ratio = 1, steam-to-carbon molar ratio = 4, GHSV = 60000 h^{-1}

much lower selectivity of C_2H_4 . Since C_2H_4 is a typical precursor of polymerized condensation resulting in carbon deposition, the lower selectivity of C_2H_4 links to the better stability against coking. Introduction of oxygen could relieve the deactivation by coking and improve the thermodynamic equilibrium conversion of reaction system³. Therefore, all the catalysts displayed the higher activity in OSRG. Meanwhile, $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ still performed the best. It is worth pointing out that $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ also presented very high yield of H_2 . In the case of OSRG, the H_2 STY value could reach $13.4\text{ L}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. In the case of SRG, a very high STY value could be reached at $21.6\text{ L}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, which is much higher than most of literature³⁵. According to the results of catalyst characterizations, two reasons may be responsible for the high performance of $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$, detailed as follows: (i) the existence of La_2O_3 could increase the dispersity of metallic Ni and enhance the MSI, thus suppress the sintering of metallic Ni particles; (ii) the lattice oxygen from CeO_2 could inhibit the coke formation and facilitate the removal of coke simultaneously on the catalyst surfaces. The substitution of La for Ce would improve the amount of the surface oxygen. However, the excessive La would decrease the activity due to the decreased lattice oxygen, specific surface area and pore volume. This has also been proved by Xu *et al.*²².

The $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ catalyst was subjected to a long-term stability test for 210 h. As shown in Fig.7, $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ showed an excellent stability, indicated by the high conversion of glycerol above 95% and the steady production of H_2 -enriched gas with about 85% H_2 selectivity (~50% purity) during the 210 h time on stream. At the meantime, the concentrations of CH_4 and C_2H_4 stayed very low (less than 0.3%). The aforementioned results demonstrated that the $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ catalyst can be used as an efficient and stable material for reforming glycerol to produce hydrogen-enriched gas.

4 Conclusions

We synthesized $\text{Ce}_x\text{Ni}_{0.5}\text{La}_{0.5-x}\text{O}$ catalysts utilizing Ce and La composite oxides as carrier *via* co-precipitation method and studied the effect of Ce to La ratios on the catalytic performance

in reforming glycerol for hydrogen production. Catalyst characterizations indicate that La_2O_3 could disperse and stabilize Ni particles. The substitution of La for Ce would increase the amount of the oxygen species on catalyst surfaces. The synergy of La_2O_3 and CeO_2 could prevent the Ni-based catalyst from deactivation caused by the sintering and coke deposition. $\text{Ce}_{0.4}\text{Ni}_{0.5}\text{La}_{0.1}\text{O}$ was the optimal catalyst, because of the highest lattice oxygen concentration, surface area, the strong MSI and the smallest Ni particle size. The conversion of glycerol retained no change above 95% and the H_2 concentration was maintained around 50% in a long-term stability test for 210 h. Our work suggests the Ce-La composite is promising as a support of Ni-based catalysts to achieve a highly efficient and stable catalyst for the OSRG reaction.

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