



Article Hydrogen Production from Chemical Looping Reforming of Ethanol Using Ni/CeO₂ Nanorod Oxygen Carrier

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Abstract: Chemical looping reforming (CLR) technique is a prospective option for hydrogen production. Improving oxygen mobility and sintering resistance are still the main challenges of the development of high-performance oxygen carriers (OCs) in the CLR process. This paper explores the performance of Ni/CeO₂ nanorod (NR) as an OC in CLR of ethanol. Various characterization methods such as N₂ adsorption-desorption, X-ray diffraction (XRD), Raman spectra, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), H₂ temperature-programmed reduction (TPR), and H₂ chemisorption were utilized to study the properties of fresh OCs. The characterization results show the Ni/CeO₂-NR possesses high Ni dispersion, abundant oxygen vacancies, and strong metal-support interaction. The performance of prepared OCs was tested in a packed-bed reactor. H₂ selectivity of 80% was achieved by Ni/CeO₂-NR in 10-cycle stability test. The small particle size and abundant oxygen vacancies contributed to the water gas shift reaction, improving the catalytic activity. The covered interfacial Ni atoms closely anchored on the underlying surface oxygen vacancies on the (111) facets of CeO₂-NR, enhancing the anti-sintering capability. Moreover, the strong oxygen mobility of CeO₂-NR also effectively eliminated surface coke on the Ni particle surface.

Keywords: chemical looping reforming; hydrogen; oxygen carrier; CeO₂; nanorod

1. Introduction

Hydrogen is considered an efficient energy carrier that is environmentally benign [1]. Chemical looping reforming (CLR) is a prospective alternative for hydrogen production due to its energy efficiency and inherent CO₂ capture [2,3]. The fixed-bed reactor configuration CLR process (Figure 1) is performed by alternatively switching the feed gases; the oxygen carriers (OCs) are stationary and periodically exposed to redox atmosphere [4]. The key to developing a CLR process is to screen high-performance OCs. Ni-based OCs have been widely investigated because of their ability for carbon–carbon and carbon–hydrogen bonds cleavage [5–7]. Zafar et al. [8] prepared a series of OCs including Fe, Cu, Mn, and Ni supported by SiO₂ and MgAl₂O₄ and concluded that NiO supported on SiO₂ exhibited high H₂ selectivity in CLR. Löfberg et al. [9] demonstrated that Ni plays two essential roles in CLR process, i.e., the anticipated activation of reactants as well as the regulation of the oxygen supply rate from solids. Dharanipragada et al. [10] reported that the Ni-ferrites OC suffers from the loss of oxygen storage capacity due to Ni sintering in chemical looping with alcohols. Improving oxygen mobility and sintering resistance remain the major challenges of the development of Ni-based OCs in the CLR process due to the high activation energy of oxygen anion diffusion in NiO (2.23 eV in CLR) and the low Tammann temperature of Ni (691 °C) [11–14].



Figure 1. Schematic description of CLR of ethanol.

Recent research has revealed that CeO₂ exhibits excellent redox property due to abundant oxygen storage capacity and the strong capability to stabilize Ni nanoparticles because of strong metal support interaction (MSI) [15,16]. CeO₂ can readily release lattice oxygen under reducing conditions, thus creating oxygen vacancies which are associated with oxygen mobility [17]. The MSI between the Ni and CeO₂ could tune the physiochemical properties of Ni, contributing to high catalytic reactivity and stability [18]. Jiang et al. [19] proposed that the oxygen vacancies of CeO₂ could effectively eliminate surface coke deposition, activate steam, and shorten the "dead time" in the CLR process. Dou et al. [20] revealed that the surface oxygen originating from the CeO₂ lattice can oxidize coke precursors, keeping the OC surface free of coke deposition. It has been reported that MSI and the mobility of lattice oxygen show strong dependence on the morphology of CeO₂ [21]. Lykaki et al. [22] have demonstrated CeO₂ morphology dominates reducibility and oxygen mobility, which follow the sequence: nanorod (NR) > nanopolyhedra (NP) > nanocube (NC). Moreover, the apparent activation energy of these three CeO₂ shapes for the CO oxidation in a hydrogen-rich gas shows the opposite trend, implying the potential highest water gas shift (WGS) activity of NR [23].

Therefore, in this work, a Ni/CeO₂-NR OC for CLR of ethanol for hydrogen production is prepared by a hydrothermal method. The physicochemical properties are investigated by N₂ adsorption-desorption, X-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES), Raman spectra, high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and H₂ temperature-programmed reduction (H₂-TPR). The performances of the Ni/CeO₂-NR OC are tested in a packed-bed reactor and compared with the other reference bulk OC, i.e., Ni/CeO₂.

2. Results and discussion

2.1. Characterization of OCs

Predominant physicochemical properties of fresh Ni/CeO₂-NR and CeO₂-NR are tabulated in Table 1. The introduction of Ni species has a pronounced influence on the texture of CeO₂-NR. The CeO₂-NR support showed higher Brunauer-Emmett-Teller (BET) surface area than that of Ni/CeO₂-NR. The average pore diameter and pore volume also exhibited the same trends. It has been reported that the BET surface of CeO₂-NR decreased by 13–18% after the incorporation of 7.5 wt % CuO [22]. The actual Ni content of Ni/CeO₂-NR determined by ICP-OES was 9.7 wt %.

Sample	Surface Area	Average Pore	Pore Volume	Ni Content	Ni Dispersion	Ni Crystal Size/Ni	CeO ₂ Crystal
	(m ² /g)	Diameter (nm)	(cm ³ /g)	(wt %)	(m²/g _{Ni})	Average Particle Size (nm)	Size (nm)
Ni/CeO ₂ -NR	75.1	18.2	0.37	9.7 ¹	6.5 ²	8.9 ³ /8.1 ⁴	16.1 ³
CeO ₂ -NR	90.3	26.5	0.80	N/A	N/A	N/A	14.8

Table 1. Physicochemical properties of fresh Ni/CeO₂-NR and CeO₂-NR.

^{1.} Determined by ICP-OES; ^{2.} Determined by H₂ chemisorption; ^{3.} Determined by XRD from Ni (111) and CeO₂ (111) plane; ^{4.} Calculated from the HRTEM images.

The XRD profiles of fresh Ni/CeO₂-NR and CeO₂-NR OCs are shown in Figure 2. The reflection peaks at 28.5°, 33.1°, 47.5°, 56.3°, 59.1°, 69.4°, 76.7°, and 79.1° could be indexed to (111), (200), (220), (311), (222), (400), (331), (420), and (422) planes of a fluorite-structure CeO₂ (Space group: *Fm3m*), respectively. There were no other impurity peaks of the hexagonal structure of Ce(OH)₃ or Ce(OH)CO₃ detected, indicating the excellent crystalline purity of CeO₂. Two peaks at 44.5° and 51.8°, which could be respectively attributed to (111) and (200) facets of Ni, were observed for Ni/CeO₂-NR. The mean crystal sizes of Ni and CeO₂ were obtained from the Scherrer Equation (listed in Table 1). The crystal sizes of CeO₂ for CeO₂-NR and Ni/CeO₂-NR were 14.8 and 16.1 nm, respectively, indicating that the incorporation of Ni would not significantly change the structure characteristics of CeO₂ support. Similar crystallite sizes of CeO₂-NR prepared by the hydrothermal method have been reported in other work [22,24].



Figure 2. XRD profiles of Ni/CeO₂-NR and CeO₂-NR.

Raman spectroscopy was employed to characterize surface and bulk defects. As shown in Figure 3, both samples present four characteristic peaks. The appreciable peak at 462.8 cm⁻¹ resulted from the first order F_{2g} mode of the fluorite cubic structure. The Raman shift at 596.1 cm⁻¹ could be assigned to the defect-induced band (D band). The relocation of O atom from the interior of tetrahedral cationic sub-lattice to the interior of ideally empty octahedral cationic sites (Frenkel interstitial sites) would lead to the deformation of the anionic lattice of CeO₂ [25]. The intensity of the D band is a gauge of the distortion of ionic lattice, which results in punctual defects and oxygen vacancies [22]. Therefore, the value of $I_D/I_{F_{2g}}$ is commensurate with the number of defect sites in ceria. The relative intensity of $I_D/I_{F_{2g}}$ decreased after the incorporation of Ni, suggesting NiO species suppress the surface oxygen vacancy of CeO2-NR. Li et al. [26] reported that Vanadium atom would bond to the surface of CeO₂-NR by generating V–O–Ce species, thus covering oxygen defects and stabilizing adjacent Ce atoms. The inconspicuous peak at 258.1 cm⁻¹ results from the second order transverse acoustic mode (2TA) or doubly degenerate transverse optical mode (TO), which are Raman inactive in a perfect crystal [27]. The peak at 1179.9 cm^{-1} may be related to the stretching mode of the short terminal Ce=O. Moreover, the Raman shift of Ni/CeO₂-NR moved towards a low wavenumber in comparison with that of CeO₂-NR, indicating the incorporation of Ni affects the symmetry of Ce–O bonds [21].



Figure 3. Visual Raman spectroscopy of Ni/CeO₂-NR and CeO₂-NR.

The TEM of CeO₂-NR and Ni/CeO₂-NR are illustrated in Figure 4. The Ni/CeO₂-NR maintained the original nanorod shape after Ni incorporation. The CeO₂-NR was approximately 14 nm in diameter and several hundreds nm in length. As shown in Figure 4a, the calculated interference fringe spacings (d) are 0.27 and 0.31 nm, revealing the CeO₂-NR predominantly exposes the (100) and (111) facets. The preferable exposure crystal facets of CeO₂-NR are consistent with those of samples derived from the CeCl₃ precursor in other studies [28,29]. Theory calculation has demonstrated that the (111) is the least reactive facet, followed by (100) and (110). In addition to the preferable crystal facets, there are other aspects degerming CeO₂ activity. Several 'dark pits' are shown in the box of Figure 4. Liu et al. [29] have reported that these dark pits are related to the surface reconstruction and defects; their study also concluded that these defects play a more important role in determining the CeO_2 activity than the exposure planes. Sayle et al. [30] have performed a molecular dynamic modeling to simulate the synthesis of CeO₂-NR and discovered that the atomistic sphere model exhibits many steps on the (111) planes of CeO_2 -NR. The migration of oxygen in CeO_2 occurs by a vacancy hopping mechanism; therefore, the clusters of defects are conducive to oxygen transfer. If the diffusion rate of oxygen anions becomes adequately high, a consecutive oxygen flow is generated, resulting in high reducibility. The Ni particle size distribution, which is calculated from 52 particles, was inserted in Figure 4, and the average particle size was 8.1 nm (shown in Table 1). Shen et al. [31] have elucidated that the strong interfacial anchoring effect, which exists between the surface oxygen vacancies on (111) planes of CeO₂-NR and the gold particles, only allows the gold particles to locally rotate or vibrate but not to migrate to form aggregates. Therefore, the strong MSI would significantly improve the Ni dispersion on the CeO₂-NR surface, resulting in a small particle size of Ni.



Figure 4. (a) HRTEM image of CeO₂-NR, (b) TEM image of CeO₂-NR, (c) and (d) TEM images of Ni/CeO₂-NR.

XPS was employed to investigate the valences of Ce and Ni cations. The XPS spectra of Ce 3d of Ni/CeO₂-NR (shown in Figure 5a) could be deconvoluted into two spin-orbit series, i.e., $3d_{5/2}(u)$ and $3d_{3/2}(v)$. The multiplet splitting components labeled u^0 , u^1 , u^2 , v, v^1 and v^2 corresponds to the $3d^{10}4f^0$ state of Ce⁴⁺, while the u_0 and v_0 are related to $3d^{10}4f^1$ state of Ce³⁺. These two Ce species in Ni/CeO2-NR indicate the OC surface was partly reduced because of oxygen desorption and the formation of oxygen vacancies. It is widely accepted that oxygen vacancies are produced to maintain electrostatic balance once Ce^{3+} exists in fluorite Ce (Equation 1). The percentage of Ce^{3+} cations to the total Ce cations is determined by the area ratio of different Ce species in XPS spectra. The Ce³⁺ ratio of Ni/CeO₂-NR (16.9%) was lower than that of pure CeO₂-NR (24.3%) reported in Lykaki et al. [22], suggesting NiO species could inhibit the formation of surface-unsaturated Ce³⁺. The decrease in surface Ce³⁺ species of Ni/CeO₂-NR was consistent in the trend of $I_D/I_{F_{2\sigma}}$ in the Raman result. The Ni 2p XPS spectra (illustrated in Figure 5b) were characterized by two spin-orbit groups, i.e., 2p_{3/2} (855.2 and 856.4 eV) and 2p_{1/2} (873.3 eV), as well as a shake-up peak at 861.8 eV. The photoelectron peak of 2p_{3/2} over Ni/CeO₂-NR shifted towards high-binding energy in contrast to those over pure NiO (844.4 eV, reported in Lemonidou et al. [32]) and Ni/CeO₂ (854.5 eV, reported in Tang et al. [33]). This result implies there is an enhanced MSI between Ni and CeO₂-NR. The Ni/Ce atom ratio of the outer surface of CeO₂-NR (0.49) is higher than the nominal one (0.32), suggesting a Ni species enrichment from bulk to surface.

$$4Ce^{4+} + O^{2-} \to 4Ce^{4+} + \frac{2e^{-}}{\delta} + 0.5O_2 \to 2Ce^{4+} + 2Ce^{3+} + \delta + 0.5O_2 \tag{1}$$

where δ represents an empty position derived from the removal of O²⁻ from an oxygen tetrahedral site (Ce₄O).



Figure 5. (a) XPS spectra of Ce 3d; (b) XPS spectra of Ni 2p.

H₂-TPR was performed to investigate MSI. As illustrated in Figure 6, the H₂-TPR patterns of CeO₂-NR are comprised of two reduction peaks. An inconspicuous peak at 262 °C, which can be assigned to the reduction of surface-adsorbed oxygen, was observed, while a broad peak ranging from 400 °C to 550 °C could be ascribed to the reduction of Ce⁴⁺ to Ce³⁺ [22,34]. With regard to Ni/CeO₂-NR, the TPR profiles consisted of three peaks. The small peak at 220 °C may have been attributable to the reduction of the NiO species, which slightly interacted with CeO₂-NR supports. Zhang et al. [21] have reported that this NiO species is characterized by small radius and could incorporate into CeO₂-NR surface. The second peak at 356 °C could be ascribed to the reduction of NiO species, with a strong interaction with CeO₂-NR supports. The H₂ consumption of the second peak was highest among the three peaks, indicating most of the NiO strongly interacted with the support. The third peak at 494 °C was also attributed to the reduction of Ce⁴⁺ to Ce³⁺. However, the broad reduction peak of Ni/CeO₂-NR shifted to a lower temperature than that of pure CeO₂-NR, suggesting the introduction of Ni improves the reducibility of CeO₂-NR. It has demonstrated that the promoted reduction behavior is caused by the generated Ni-Ce-O species which improves the deformation of CeO₂ [35].



Figure 6. H₂-TPR patterns of Ni/CeO₂-NR and CeO₂-NR.

2.2. Activity Tests of OCs

The activity of Ni/CeO₂-NR was tested in CLR of ethanol and compared with Ni/CeO₂. Figure 7 displays the performance of both OCs in CLR: H₂ selectivity and ethanol conversion at the fuel feed step as well as the concentration of CO, CO₂ and O₂ at the air feed step. The H₂ selectivity and ethanol conversion of both OCs remained relatively stable during the process. With regard to Ni/CeO₂-NR, the average ethanol conversion remained at 88.0%, and the average H₂ selectivity was 78.9%. However, with the average ethanol conversion and H₂ selectivity of conventional Ni/CeO₂ at 72.9% and 60.5% respectively, the activity of Ni/CeO₂-NR was superior to the Ni/CeO₂. As the Ni content and other experimental conditions were the same for both OCs, the improved activity therefore resulted from the support.



Figure 7. Activity tests of (**a**) Ni/CeO₂-NR and (**b**) Ni/CeO₂.

Various factors contributed to the enhanced catalytic activity. Notably, the CeO₂-NR with high specific-to-volume ratio guarantees excellent Ni dispersion, as evidenced by TEM and TPR results. Such a one-dimensional nanostructure enables uniform and small Ni nanoparticles to be finely dispersed on supports, thus generating many accessible catalytic active sites. Additionally, the high concentration oxygen vacancies of CeO₂-NR, which was proven via Raman and XPS analysis, can activate and produce OH groups from steam. H₂ and CO₂ can be generated via the reaction between the formed OH groups as well as intermediate species, thus improving H₂ selectivity. It has been proposed that the interface of the metal/CeO₂ is the main site for steam reforming reaction [36].

The air feed process is highly oxygen consuming and is accompanied by the generation of CO_2 and CO due to coke oxidation and partial oxidation. As illustrated in Figure 7, all the samples exhibited CO_2 and CO evolution at the air feed stage. The integration areas of C-containing gas concentrations corresponded to the quantity of carbon deposition. Ni/CeO₂-NR exhibited small peak areas compared with the Ni/CeO₂ OC, indicating that the carbon deposition on Ni/CeO₂-NR was effectively suppressed. This is a result of the abundant oxygen vacancies and its strong oxygen storage capacity, which enhanced the oxygen mobility and thereby facilitated the removal of carbon deposition. In addition, the depleted CeO₂-NR could be partially replenished by the air feed step. The O₂ concentration increased from 0% to 23% at the end of the air feed stage, indicating the end of coke elimination and replenishment of lattice oxygen.

2.3. Stability Tests

The durability of Ni/CeO₂-NR and Ni/CeO₂ was tested in a 10-cycle CLR process. As shown in Figure 8, the H₂ selectivity of Ni/CeO₂ slowly declined with the increase of the running cycles, while the Ni/CeO₂ NR maintained its activity throughout the test. During the tests, the H₂ selectivity of Ni/CeO₂-NR decreased from 81.7% to 79.2%, while Ni/CeO₂ exhibited a significant decrease in H₂

selectivity from 61.8% to 51.4%. The deactivation of OCs predominantly caused Ni sintering and carbon deposition. Notably, the Ni/CeO₂-NR OC exhibited a more durable performance than the Ni/CeO₂, revealing that the CeO_2 -NR supported metal was more resistant to deactivation. The superior durability of the Ni/CeO₂-NR sample resulted from the strong MSI between Ni and CeO₂-NR support, which improved the metal-sintering resistance. The abundant oxygen vacancies of CeO₂-NR are essential units for the anchoring of metal particles. The essential role of CeO_2 is to disperse and stabilize Ni particles over its surface oxygen vacancies, which depend on the morphology of CeO_2 . As evidenced by XPS, the (111) plane of CeO₂-NR plays an important role in anchoring the Ni particles. It has been proposed that the interfacial Au atoms which are located away from the particle perimeter (covered interfacial atoms) would closely interact with the underlying surface oxygen vacancies on the (111) facets of CeO₂-NR [31]. Because this interfacial region was not involved in the reforming reaction, this strong interaction would effectively stabilize the Ni particles on CeO₂-NR. Additionally, small size Ni particles can lower the driving force for coke diffusion and thereby help to reduce the carbon deposition. Furthermore, the strong oxygen mobility of CeO₂-NR is indispensable to removing the carbon deposition at the metal surface. It has been demonstrated that the oxygen deposited in CeO₂ lattice can react with the carbon species left over from the steam reforming reaction [37]. Overall, CeO₂-NR support not only promotes the anti-sintering capability of OCs but also reduces the carbon deposition, thus improving the durability of OCs. A comparison of several investigations regarding CLR over different Ni-based OCs is tabulated in Table 2. The Ni/CeO₂-NR in this work showed higher average fuel conversion in long-term tests despite the low Ni loading, indicating the strong sintering resistance and high reforming activity of this OC.



Figure 8. Stability tests of OCs.

Table 2. Comparison	of CLR over	different OCs.
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OCs	Ni Loading (wt %)	T (°C)	S/C	Tested Cycles	Reactant	Average Conversion (%)	Average H ₂ Yield (%)	References
CeNi/MCM-41	6	650	1.5	10	Glycerol	~90	6.2	[37]
LaNiO ₃ /MMT	13	650	3	10	Ethanol	~90	-	[3]
Ni/MMT	19.9	650	4	20	Ethanol	~78	-	[13]
CeNi/PSNT	24.7	650	3	10	Glycerol	~100	12.5	[19]
CeNi/SBA-15	12	650	3	14	Ethanol	~84	-	[20]
Ni/CeO2-NR	9.7	650	4	10	Ethanol	~90	-	This work

3. Materials and Methods

3.1. Preparation of OCs

CeO₂-NR was synthesized on the basis of our previous work with small modifications [38]. Firstly, 1 g of CeCl₃ (99.9%, Aladdin, Shanghai, China) and 19.3 g of NaOH (97%, Aladdin) were dissolved in 50 mL deionized water and continuously stirred for 25 min. The resulting mixture was then put into a Teflon-lined autoclave and kept at 100 °C for 24 h. Subsequently, the sample was separated, washed, then dried at 85 °C for 10 h and finally calcined at 400 °C for another five hours. The Ni/CeO₂-NR oxygen carrier was synthesized by a wet-impregnation method. Ni(NO₃)₂·6H₂O (98%, Aladdin) of 0.2 g, equivalent to 10 wt % Ni loading, was first dispersed in 5 mL deionized water, and the prepared CeO₂-NR of 0.5 g was added into the solution. The mixture was stirred under sonication for three hours at 60 °C and then dried at 85 °C for 10 h. The as-synthesized sample was then calcined at 700 °C for two hours.

The other reference bulk Ni/CeO₂ was also synthesized by a wet-impregnation method, and the procedure has been reported in Xu et al. [39]. The Ni content of this OC was also set to 10 wt %.

3.2. Characterization of OCs

The texuture of OCs were analyzed by a Micrometric Acusorb 2100E apparatus (Ottawa, ON, Canada) at 77 K. The OCs were degassed at 573 K for three hours before tests.

ICP-OES (Nijmegen, The Netherlands) was applied to measure the elemental composition. Before tests, the sample was solved by hydrofluoric acid solution.

XRD was performed, using a Shimadzu XRD-600 instrument (Kyoto, Japan), to identify the phase composition. The scanning 2θ degrees ranged from 10° to 80° , and the scanning rate was set to 4° /min. A graphite-filtered Cu K α radiation ($\lambda = 1.5406$ Å) was applied as a radiation source.

Raman spectra were employed by a Renishaw Spectroscopy (Gloucestershire, UK) with a visible 514 nm Ar-ion laser under ambient conditions. During the mesurement, the flowing gas was He, and the test temperature was maintained at 300 °C.

TEM was conducted, using FEI Tecnai F30 (Cleveland, OH, USA), to investigate the morphology of the Ocs. The samples were first solved in ethanol under sonication, followed by dispersal on a copper grid-supported carbon foil and dried in air.

XPS was carried out by a ThermoFisher K-Alpha system with a 150 W Al K α source (Waltham, MA, USA). The samples were placed on the holder, and the scanning step was set to 0.15 eV.

H₂-TPR was employed by a Micrometrics AutoChem 2920 instrument (Ottawa, ON, Canada). In a typical procedure, a sample of 90 mg was preheated at 450 °C for one hour in an Ar flow of 35 mL/min and subsequently cooled to 80 °C. A mixture of 10 vol % H₂ in Ar flow (35 mL/min) was then inserted, and the temperature was increased from 80 °C to 100 °C at a rate of 5 °C/min simultaneously. H₂ chemisorption was also performed by the same apparatus to analyze the Ni dispersion. The sample was first reduced at 700 °C in a H₂/Ar flow (30 mL/min) for one hour, followed by cooling to 100 °C under Ar flow. Subsequently, H₂ pulses were introduced until the eluted peaks of successive pulses became steady. The Ni active surface area was obtained from the H₂ adsorbption volume considering the stoichiometric ratio H_{adsorbed}/Ni_{surface} = 1 and a surface area of 6.5×10^{-20} m² per Ni atom [40].

3.3. Activity and Stability Tests

The performance of CLR of ethanol by Ni/CeO₂-NR and reference conventional bulk OCs, i.e., Ni/CeO₂, were conducted in a packed-bed reactor, whose schematic was described in our previous work [41,42]. The tested OCs of 0.5 g were loaded at the center of the quartz reactor. During a fuel feed step, an ethanol solution (4 mL/h) with a steam to carbon ratio (S/C) of four was preheated to 150 °C and then inserted into the reactor in a N₂ flow of 180 mL/min. The reacter temperature of the fuel feed step was 650 °C. An Agilent 7890A (Santa Clara, CA, USA) chromatography with two detectors,

thermal conductivity detector (TCD) and flame ionization detector (FID), was applied to verify the effluents. TCD with a TDX-01 column was applied to detect N₂, H₂, CO, CO₂, and CH₄; the FID with a Porapak-Q column was applied to measure the concentration of $C_3H_8O_3$, H₂O, and CH₃CHO. In an air feed step, the air flow was 100 mL/min, and the reaction temperature was also 650 °C. The exhausted gases were detected by another GC (Agilent 7890A) with a TCD detector. A 5A molecular sieve column was used to detect the O₂, and the TDX-01 column was applied to detect CO₂, CO, and N₂. The durations of the fuel feed step and the air feed step were 60 and 10 min, respectively. A N₂ purge process of five minutes was performed between the fuel feed step and the air feed step to eliminate the residue gas in the reactor.

The conversion and H₂ selectivity were calculated as follows:

$$X = \frac{F_{in} - F_{out}}{F_{in}} \times 100\%$$
⁽²⁾

$$S_{H_2} = \frac{1}{6} \times \frac{\text{moles } H_2 \text{ produced}}{\text{moles ethanol feed} \times X} \times 100\%$$
(3)

4. Conclusions

A Ni/CeO₂-NR OC was synthesized by hydrothermal method and tested in CLR of ethanol process in this work. H₂ selectivity of 80% was achieved by Ni/CeO₂-NR in a 10-cycle stability test. The characterization results show that the Ni/CeO₂-NR possesses high Ni dispersion, abundant oxygen vacancies, and strong MSI. The small particle size and abundant oxygen vacancies contributed to the WGS reaction, thus improving the catalytic activity. The buried interfacial Ni atoms strongly anchored on the underlying surface oxygen vacancies on the (111) facets of CeO₂-NR, therefore enhancing the anti-sintering capability. Moreover, the strong oxygen mobility of CeO₂-NR also effectively eliminated surface coke on the Ni particle surface.

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