Highly efficient steam reforming of ethanol (SRE) over CeO\textsubscript{x} grown on the nano Ni\textsubscript{x}Mg\textsubscript{y}O matrix: H\textsubscript{2} production under a high GHSV condition

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Funding information
Ningbo Bureau of Science and Technology, Grant/Award Numbers: 2012B10042 and 2012B82011; National Key R&D Program of China, Grant/Award Numbers: 2017YFB0602602 and 2017YFC0210400

Summary
Steam reforming of ethanol (SRE) over non-noble metal catalysts is normally conducted at high temperature (>600°C) to thermodynamically favour the catalytic process and carbon deposition mitigation. However, high temperature inhibits water-gas shift reaction (WGSR) and therefore restrains the yield of H\textsubscript{2} and leads to the formation of an excessive amount of CO. The modification of non-noble metal catalyst to enhance WGSR is an attractive alternative. In this study, CeO\textsubscript{x} was firstly loaded onto a nano-scaled Ni\textsubscript{x}Mg\textsubscript{y}O matrix and subsequently used as the catalyst for hydrogen production via SRE. Morphology of the catalyst materials was characterized by using a series of technologies, while H\textsubscript{2}-temperature programmed reduction (H\textsubscript{2}-TPR), CO-temperature programmed deposition (CO-TPD), and X-ray photoelectron spectroscopy (XPS), were employed to study the surface nickel, ceria clusters, and their interactions. The catalytic activity and durability of the catalyst were studied in the temperature region of 500°C to 800°C. The CeO\textsubscript{x}-coated nano Ni\textsubscript{x}Mg\textsubscript{y}O matrix exhibited an outstanding hydrogen yield of 4.82 mol/mol\textsubscript{ethanol} under a high gas hourly space velocity (GHSV) of 200 000 hour\textsuperscript{-1}. It is found that the unique Ni\textsuperscript{0}-CeO\textsubscript{x} structure facilitates the adsorption of CO on the surface and therefore promotes the effective hydrogen production via WGSR. Moreover, this modified Ni\textsubscript{x}Mg\textsubscript{y}O matrix was found to be a more robust and anticoking nanocatalyst because of reversible switch between Ce\textsuperscript{4+} and Ce\textsuperscript{3+}.

KEYWORDS
CeO\textsubscript{x}, hydrogen production, Ni\textsubscript{x}Mg\textsubscript{y}O matrix, steam reforming of ethanol, water-gas shift reaction

1 INTRODUCTION

The unique features of hydrogen, such as clean, inexhaustible, high conversion efficiency, make it a versatile energy carrier.\textsuperscript{1} Currently, fossil fuels account for more than 90% of hydrogen production. The main processes for hydrogen production include natural gas reforming and coal and heavy oil gasification,\textsuperscript{2,3} which are associated with the formation of a fair amount of CO and SO\textsubscript{x} as by-products. Along with the rise of fuel cell hybrid electric vehicles,\textsuperscript{4,5} higher purity hydrogen production from sustainable energy resources becomes particularly attractive in this regard.\textsuperscript{6} Bioethanol has been increasingly used as a fuel and is considered as a promising alternative fuel for fuel cell because of its high H/C ratio and low cost of production.\textsuperscript{7} It has the advantages of eliminating the risks and difficulties associated with the storage and transportation of...
hydrogen. Therefore, hydrogen production from steam reforming of ethanol has been widely studied. However, during the reforming of ethanol, apart from the desired water-gas shift reaction (WGSR), many other reactions may also occur, which are shown in Table 1. Operating conditions and the composition and structure of the catalyst are also found to affect the reaction pathway and product distribution.

To date, a suite of active metals (Pt, Rh, Pd, Ni, Cu, Zn, Fe) have been studied extensively as catalysts for steam reforming of ethanol (SRE). The results showed that Ni and Rh could enable the efficient hydrogen production. However, the large-scale application of Ni-based catalysts is still of challenges including carbon deposition and metallic sintering. In our previous research, the nano-structured MgO with a high specific surface area was synthesized as the supporting material of a novel Ni, MgO matrix that exhibited an outstanding reforming activity and much better coke resistance ability when compared with the Ni/Al2O3-based catalysts and other commercialized catalysts. It is reported that the supporting material, MgO, can facilitate CO2 adsorption to accelerate the rate of coke gasification. But it also leads to the formation of a high CO content in the gaseous product and relatively low hydrogen yield, which can be attributed to the inhibition of WGSR at high temperature. From a thermodynamic perspective, the desired operating temperature of SRE process is in the region of 600°C to 900°C. One of the reasons is that carbon deposition could be mitigated at high temperatures. However, moderate temperature (>600°C) will thermodynamically inhibit H2 formation via WGSR and lead to an excessive amount of CO in the product, which would hinder its further application in fuel cell. Therefore, low-temperature SRE (<400°C) is highly attractive and is usually achieved by using various noble metals such as Pt, Rh, Ru, and Pd. However, high price and low accessibility of noble metals might limit their large-scale use.

Another approach to enhance WGSR is to modify the non-noble catalyst directly. In earlier studies, it was found that the strong metal-support interaction (SMSI) inside the Ni-Ce system enabled the stabilization of Ni particles and improved the reducibility of Ni2+ ions. In fact, the spare electrons from Ce3+ could migrate to neighbouring Ni2+ ions and increase the reducibility of the subsurface Ni2+ ions. This activation of nickel sites may improve hydrogen production via the acceleration of ion exchange between CO and H2O. On the other hand, CeO2 can accelerate water dissociation to form OH− groups, which are essential for the hydrogen production from CxH and CxOxH.

To develop a robust catalyst for the in situ hydrogen production in fuel cells, in this study, nano CeOx clusters were grown over the novel Ni, MgO matrix to introduce new interactions between CeOx clusters and the restrained nickel ions inside the subsurface MgO matrix. The effect of this Ni0-CeOx over WGSR was investigated under moderate temperature (>600°C). The overall catalytic performance in SRE was also studied under a high GHSV condition with a focus on hydrogen yield and anticarbon formation ability.

2 | EXPERIMENTAL

2.1 | Preparation of catalysts

All chemicals used in this research are of analytical grade (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). Two types of catalysts, i.e., NixMgO, Ni, MgO-Ce, were prepared following the procedures described elsewhere. Firstly, magnesium nitrate and polyethylene glycol (PEG, Mn=20 000) were dissolved in deionized
water. Then, the ammonia solution (5 wt%), as a sedimentation agent, was introduced into the solution dropwise with continuous stirring. The slurry therefore formed was then transferred into a Teflon-lined vessel for hydrothermal treatment by being kept at 100°C for 24 hours. The treated slurry was subsequently filtered without washing, dried at 120°C for 24 hours, and calcined at 700°C for 6 hours. The calcined material was then impregnated with a nickel nitrate solution at 60°C, and the obtained precursor was dried and calcined following the same processes described previously.

To prepare the Ce-modified catalysts, magnesium nitrate, PEG, and cerium nitrate were initially dissolved in deionized water at a controlled molar ratio. The rest of the procedure was the same as for the preparation of the Ni₃Mg₆O catalyst.

In this study, the theoretical value of nickel loading was controlled at 10 wt% in mass, while the loading of Ce was 3 wt%, which was selected based on previous investigation on the effects of Ce loading as shown in Table S1. The denoted names and the actual compositions of individual catalysts are shown in Table 2.

### 2.2 Characterization of catalysts

N₂ adsorption-desorption experiment was carried out to show the surface morphology of the catalysts. Following the Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) procedure described elsewhere, the specific surface area, pore volume, and micropore volume of both fresh and spent catalysts were characterized by using a Micrometrics ASAP-2020. The measurements were performed at −196°C, after the degas process at 300°C for 5 hours.

Crystal structure of the catalysts was analysed by using an X-ray diffraction (XRD, Bruker D8 Advance) with a Cu X-ray tube (λ = 1.5406 Å). The diffraction intensity was recorded at a range of 2θ between 10° and 90° with a step size of 0.01° and a counting time of 1 second.

The reducibility of nickel species on the fresh catalysts was studied via H₂−temperature programmed reduction (H₂-TPR) (Finetec, Finesorb 3010D) following the process detailed elsewhere. In each test, approximately 30 mg of the catalyst was pretreated at 300°C in argon (99.999%) and then heated from room temperature to 1000°C at a heating rate of 5°C/min under a specific atmosphere (10 vol% H₂ in argon).

In order to investigate the CO adsorption onto the surface nickel, the CO-temperature programmed desorption (CO-TPD) was also carried out using the Finetec Finesorb 3010D. Approximately 70 mg of sample was reduced by H₂ at 700°C for 2 hours. The inflow gas was then switched to pure argon (99.999%) to purge off the residual H₂. Meanwhile, the bed temperature was decreased to 300°C and kept isothermal for 1 hour. The CO adsorption was conducted at room temperature for 30 minutes, followed by an argon purging process until the signal of the thermal conductivity detector (TCD) became stable. The desorption process was carried out from room temperature to 750°C at a heat rate of 5°C /min.

The amount of carbon deposited on the used catalysts was quantified using thermogravimetric analysis (TGA, NETZSCH, model STA449F3). In each test, approximately 20 mg of the catalyst was kept at 105°C for 20 minutes and then heated to 1000°C at a heating rate of 10°C /min. An accurate balance would record the weight variations of the sample accompanied by increasing of temperature.

Raman spectrum was also applied to investigate disordered and graphitized carbon on the spent catalysts at room temperature by using a Renishaw inVia reflex equipped with a 532-nm wavelength laser. Each sample was scanned from 800 to 3200 cm⁻¹ for at least three times at different positions to minimize experimental errors.

The oxidation states of elemental species on the surface of the catalysts were characterized by using X-ray photoelectron spectroscopy (XPS, Shimadzu Axs Ultra DLD Spectroscope), which was operated under a vacuum condition of 10⁻⁹ Torr. A monochromatized Al Kα radiation source was used along with the spectrum calibration of C 1s spectrum at 248.8 eV. Both reduced and spent catalysts were analysed to find out the transformation of oxidation state of the surface metals.

The texture of the catalysts and the deposited carbon were observed using a transmission electron microscope (TEM, JEOL JEM-2100F). For the sample preparation, the catalyst powder was dispersed in ethanol with 3-minute ultrasonic treatment (40 kHz) and then titrated onto 400-mesh copper grids.

### 2.3 Steam reforming experiment

The schematic of experimental setup is shown in Figure 1. During the course of testing, nitrogen (300 mL/min) was
used as a carrier gas as well as a reference for the determination of the flow rates of product gases. Prior to each test, the catalyst was activated at 700°C for 2 hours under 25 vol% H₂ in N₂ at a flow rate of 400 mL/min. The water and ethanol mixture was injected into the reaction system by using a syringe pump (Eldex Lab, Inc.) at a rate of 1 mL/min (the gaseous flow rate of ethanol and water was 134.7 mL/min and 808.1 mL/min, respectively, GHSV = 200 000 h⁻¹). The steam-to-carbon molar ratio of the liquid mixture was fixed at 3 (steam/ethanol molar ratio = 6). The liquid mixture was evaporated in a preheater (300°C) and mixed with nitrogen gas before being introduced to the reactor. The catalyst was loaded on the top of a perforated tray, which was placed in the middle of the reactor (310S stainless steel, ID = 12 mm). For each test, approximately 1.0 g of catalyst was diluted by 15.0 g of quartz sand (Aladdin, 2–3 mm φ), which was calcined prior to mixing to remove moisture and volatile contaminant. A thin layer of silica wool was placed underneath the catalyst bed to prevent the loss of the catalyst powder. A thermocouple was placed along the central axis of the reactor to monitor temperature of the catalyst bed. The outflow gas passed through a cold trap and was collected by using a 1-L Tedlar bag and was analysed offline by using a gas chromatograph (Shimadzu, GC-2014). For each catalyst, its catalytic activity was tested at four different temperature levels, ie, 500°C, 600°C, 700°C, and 800°C. The composition of gas outflow was analysed 2 hours after temperature of the catalyst bed had become stable. For the durability test, catalytic reforming was carried out at 700°C and lasted for 30 hours. All the tests were carried out under atmospheric pressure.

2.4 | Evaluation of catalytic performance

The yield of hydrogen was defined based on the stoichiometry of the SRE reaction (R1):

\[
\text{H}_2 \text{ yield (mol/mol ethanol)} = \frac{\text{mole of produced hydrogen}}{\text{mole of input ethanol} \times 6}
\]

(1)

The conversion of ethanol \(X_{\text{ethanol}}\) was calculated only based on the production of CO₂, CH₄, and CO. Other products, such as ethylene, acetaldehyde, and acetylene, were neglected because of their extremely low mole fractions in the gas product.³⁰

\[
X_{\text{ethanol}} (\%) = \frac{\text{carbon mole of total products}}{\text{mole of input ethanol} \times 2} \times 100\%
\]

(2)

The yield of carbonaceous gases, such as CO₂, CO, and CH₄, was calculated by

\[
\text{Carbonaceous gas yield (mol/mol ethanol)} = \frac{\text{mole of produced carbonaceous gas}}{\text{mole of input ethanol} \times 2}
\]

(3)

3 | RESULTS AND DISCUSSION

3.1 | N₂ adsorption-desorption analysis

Structural features of the catalysts were characterized following the BET method, the results of which are
illustrated in Table 3. It is clear that the fresh catalyst NiₓMgᵧO-Ce showed a very similar surface property to the NiₓMgᵧO catalyst, which indicates that the addition of Ce had no obvious influence on the morphology of the catalyst. This finding is also confirmed by their very similar shape of isotherms (pseudo-type II isotherm) and similar pore size distribution, as shown in Figure 2.²⁶

3.2 | XRD analysis

Figure 3A shows the XRD patterns of the fresh catalysts that NiO and MgO exhibited the same structure as NaCl. Since no double structure peaks were observed at typical patterns of NiO or MgO, this means that the NiₓMgᵧO matrix is actually a rock salt structure solid solution because of the similar ionic radius and the same valence number of Ni²⁺ and Mg²⁺ ions.¹⁶,³¹ For the fresh NiₓMgᵧO-Ce, fluorite phase of CeO₂ was observed with weak intensity, which indicates small CeO₂ particulates dispersed over the catalyst surface.²⁴,³²,³³ The immiscibility of MgO and rare earth metal oxides resulted into a weak intensity of the rock salt phase peak and increased the reducibility of surface nickel ions by altering nickel electronic property, which will affect the activity of metallic nickel clusters in SRE²⁴

3.3 | Characteristics of Ni species

The H₂-TPR analysis was carried out to study the reducibility of surface metal ions and the interactions between nickel ions and the support, the results of which are shown in Figure 4A. For the NiₓMgᵧO catalyst, the main peak (at 889°C) was attributed to the reduction of Ni²⁺ ions dissolved inside the MgO lattice to form NiₓMgᵧO solid solution.³⁴ The broad shoulder peak at 630°C or above was confirmed as the reduction of Ni²⁺ ions at sublayers in previous work.¹⁶

For the NiₓMgᵧO-Ce, it is obvious that the total reducibility of primary nickel specie (around 884°C) decreased after the doping with the promoter, which suggests that surface-isolated CeO₂ could consume surface hydrogen gas and hinder hydrogen from penetrating into the matrix of solid solution for Ni²⁺ reduction.³⁵ The broad shoulder peak near 730°C could also be explained as the reduction of Ni²⁺ at sublayers,²⁴,³⁴ which was similar with the situation of the shoulder peak of the NiₓMgᵧO at 630°C. These broad shoulder peaks could also be attributed to the reduction of CeO₂ particles dispersed on the surface.³⁶,³⁷ Moreover, there is a noticeable broad peak at the low-temperature region of 300°C to 550°C. The existence of this reduction peak could be explained by two reasons. The first reason is the direct reduction of surface CeO₂ particles. At this temperature, CeO₂ particles can be reduced

| Catalysts         | Surface Area, m²/g | Pore Volume, cm³/g | Micropore Volume, cm³/g | Pore Size, nm |
|-------------------|--------------------|--------------------|------------------------|---------------|
| Fresh NiₓMgᵧO     | 56                 | 0.28               | 0.0059                 | 20            |
| Used NiₓMgᵧO      | 138                | 0.47               | 0.0090                 | 14            |
| Fresh NiₓMgᵧO-Ce  | 52                 | 0.29               | 0.0045                 | 22            |
| Used NiₓMgᵧO-Ce   | 37                 | 0.12               | 0.0024                 | 13            |

FIGURE 2 N₂ physisorption characterization. A, Adsorption-desorption isotherms. B, Pore size distribution [Colour figure can be viewed at wileyonlinelibrary.com]
from Ce$^{4+}$ to Ce$^{3+}$ by H$_2$. On the other hand, the reduced CeO$_2$ particles could provide extra electrons that migrate to the neighbouring nickel sites or subsurface nickel merged inside MgO matrix and make Ni$^{2+}$ ions much easier to be reduced. The second reason is the reduction of the uncovered Ni$^{2+}$ ions at the outermost layer with square pyramidal coordination or the reduction of NiO that has no interaction with the MgO surface. In order to further investigate the reason behind this, XRD experiment was conducted again to investigate the reduced catalysts, which were treated in a flow of 25 vol% H$_2$ in N$_2$ at 700°C for 2 hours.

As shown in Figure 3B, no peaks for the reduced Ni$^0$ were observed in the XRD pattern of the reduced Ni$_x$Mg$_y$O. However, in the TPR pattern of the Ni$_x$Mg$_y$O, low-intensity humps in the temperature range of 300°C to 550°C were observed, and it could be only ascribed to the existence of a small amount of Ni$^{2+}$ ions over the...
The reason for such could be that Ni\textsuperscript{0} particles were highly dispersed on the internal surface of the support or the formation of small size Ni\textsuperscript{0} crystals (<5 nm), which cannot be detected by XRD analysis.\textsuperscript{41,42} For the Ni\textsubscript{x}Mg\textsubscript{y}O-Ce, it was different from the Ni\textsubscript{x}Mg\textsubscript{y}O catalyst that Ni (220) peak was found near 76.1°. Combined with the XPS results (shown in Figure S1), in which the reduction of CeO\textsubscript{2} was detected, it could be speculated that surface CeO\textsubscript{2} is reduced under reducing atmosphere and form vacancies. These vacancies make the reduced CeO\textsubscript{x} particles more wettable to the neighbouring nickel sites and accelerate the formation of metallic nickel particles on the surface and lead to a new Ni\textsuperscript{x}-CeO\textsubscript{y} structure.

### 3.4 CO-TPD analysis

It is reported that the site for CO adsorption is Ni crystal but not the MgO support.\textsuperscript{43} In this study, CO-TPD was carried out to find out the interactions between Ni sites and CO molecules. In Figure 4B, the desorption peaks observed over the Ni\textsubscript{x}Mg\textsubscript{y}O solid solutions could be divided into three groups. The peaks at low temperatures (<200°C) are ascribed to desorption of CO molecules with weak bonds from the smooth nickel crystal planes (α site).\textsuperscript{38,44} The second peak group, located in a higher temperature region (200°C-350°C), could be attributed to more strongly bonded CO molecules.\textsuperscript{38} The broader peaks, desorbed at temperatures above 400°C, are associated with the CO dissociative adsorption over the stepped nickel surface (β site).\textsuperscript{43} Moreover, the broad peaks above 400°C could also be attributed to the formation of CO\textsubscript{2} because of oxidation of the adsorbed CO by the subsurface metal oxides or the product from WGSR of CO and surface hydroxyl groups.\textsuperscript{43,45,46} Comparing two catalysts, the amount of CO desorbed at low temperatures (<400°C) did not vary significantly because of their similar surface nickel content. However, the Ni\textsubscript{x}Mg\textsubscript{y}O-Ce showed much higher intensity peak above 400°C; it confirmed that the addition of CeO\textsubscript{2} facilitates the adsorption of CO at higher temperature. Moreover, higher capability of CO adsorption promotes the WGSR and results in a higher H\textsubscript{2} production.

### 3.5 Catalytic performance in SRE

#### 3.5.1 Hydrogen yield and ethanol conversion

Hydrogen yield is a vital parameter for the evaluation of catalytic performance in steam reforming. In theory, 1 mol of ethanol can produce 6 mol of H\textsubscript{2}. However, some hydrogen molecules might participate in methanation reaction (the reverse of R12), and WGSR (R9) might be inhibited at a certain extent because of high-temperature condition. As shown in Figure 5A, the Ni\textsubscript{x}Mg\textsubscript{y}O catalyst showed relatively low selectivity in hydrogen yield. At lower temperatures, for instance, 500°C, the Ni\textsubscript{x}Mg\textsubscript{y}O catalyst only resulted in a H\textsubscript{2} yield of 0.75 mol/mol\textsubscript{ethanol}, while the Ni\textsubscript{x}Mg\textsubscript{y}O-Ce catalyst had considerably higher H\textsubscript{2} yields of 2.47 mol/mol\textsubscript{ethanol}. At higher temperatures, such as 600°C, 700°C, and 800°C, the initial H\textsubscript{2} yields of the modified catalyst were all above 4.70 mol/mol\textsubscript{ethanol}, while the highest yield for the Ni\textsubscript{x}Mg\textsubscript{y}O catalyst was only 3.34 mol/mol\textsubscript{ethanol} at 800°C. Thus, the actual experiment result verified the promoting effects of nanoceria addition.

For the conversion of ethanol, it is clear (as shown in Figure 5B) that the Ni\textsubscript{x}Mg\textsubscript{y}O catalyst showed a much lower ethanol conversion of 21.5% at 500°C if compared with Ni\textsubscript{x}Mg\textsubscript{y}O-Ce, which had a more than double conversion of 49.8%. This result is consistent with their hydrogen yield. On the contrary, the ethanol conversion of the Ni\textsubscript{x}Mg\textsubscript{y}O catalyst at temperatures above 600°C was inhibited at a certain extend because of high-temperature condition.
on a similar level as the modified catalyst. The possible reason for such could be that the temperature above 600°C is high enough to thermodynamically favour the decomposition of ethanol.11

3.5.2 Durability test

The long-term tests were carried out at 700°C for 30 hours, and the results are shown in Figure 6. Normally, the catalytic activity of steam reforming catalyst decreases as a result of metal sintering (causing decreasing of active surface area) and carbon deposition (causing encapsulation of active metal particles) coupling with the blockage of surface defects.47,48 In this study, hydrogen yield and ethanol conversions of both catalysts increased at the initial stage of the reaction, and they showed even higher hydrogen yield rates at the final stage of the long-term tests. The reason for this observation could be the slow reduction of the active metal oxide (NiO) from the support matrix. At the early stage of the SRE, most of the nickel ions were still in their oxidized state (Ni²⁺) and dispersed inside sublayers of the Ni₇Mg₃O matrix, which were not reduced to Ni⁰ during the hydrogen reduction process. Therefore, more newly reduced Ni⁰ sites formed when the SRE process proceeded, which resulted in the formation of more active sites and subsequently led to higher H₂ yields. This deduction was also confirmed by the comparison of XRD patterns of the reduced catalysts and the spent catalysts after long-term SRE tests as shown in Figure 3B,C. It was found that the XRD spectrums of the reduced catalysts showed no Ni⁰ diffraction peaks but appeared in the spent catalysts.

In general, both catalysts did not show notable deactivation during the long-term tests, and the distribution of products did not vary significantly. The Ni₇Mg₃O-Ce catalyst showed a high efficiency in hydrogen production with a yield of 4.82 mol/mol ethanol, which was achieved in extremely high GHSV (200 000 h⁻¹) applied in this study.

In Table 4, the Ni₇Mg₃O-Ce catalyst is also compared with many other nickel-based catalysts from recent literatures.49-54 It is noteworthy that the Ni/Y₂O₃ catalyst was the only catalyst, which showed higher hydrogen yield at 5.25 mol/mol ethanol, while its space velocity was only one-twentieht of what was applied to Ni₇Mg₃O-Ce in this study.

3.5.3 Evolution of gas yields

From Figure 6, it can be observed that the Ni₇Mg₃O had higher ethanol conversion but lower hydrogen production. The reason behind this was further investigated by comparing the carbonaceous gas yields. For the modified catalyst, the Ni₇Mg₃O-Ce had different tendency in the yield of gas products. It showed lower methane yield, which suggested that the pathways for the formation of methane were suppressed. These pathways included methanation reaction (the reverse of R10), direct decomposition of acetaldehyde (R6), and surface carbon hydrogenation (the reverse of R12). It can also be deduced that steam reforming of acetaldehyde (R5) was more favoured to produce H₂. On the other hand, the surface carbon and CO were also favoured to be oxidized by the surface oxygen from CeO₂ instead of the hydrogenation to produce methane.55 Therefore, these reaction pathways restricted the formation of methane and indirectly contributed to a higher hydrogen yield. Apart from the difference in methane yield, the Ni₇Mg₃O-Ce catalyst also had higher CO₂ yield and lower CO yield, which indicated that WGSR was enhanced to produce more hydrogen. The results of CO-TPD test in this study also proved that the addition of Ce enhanced the adsorption of CO over surface nickel to promote the WGSR. From the point view of the WGSR mechanism, the adsorbed CO on the surface nickel sites can be easily oxidized to CO₂ by the vicinal CeO₂ particles. Then, the reduced CeOₓ captures oxygen from the

![FIGURE 6](https://wileyonlinelibrary.com) Product yields and ethanol conversion versus time on stream: (A) Ni₇Mg₃O, (B) Ni₇Mg₃O-Ce (reaction conditions: 700 °C, S/C = 3, GHSV = 200 000 h⁻¹, P = 1 atm) [Colour figure can be viewed at wileyonlinelibrary.com]
dissociation of water to production H₂. In other words, ceria helps the generation of OH\(^-\) groups via the decomposition of water molecule. The OH\(^-\) groups can also promote the formation of H₂ and CO₂ from CₓH and CₓOₓH species.\(^{26}\) Therefore, the Ni\(^0\)–CeO\(_x\) system facilitates hydrogen production via the promotion of CO adsorption and the dissociation of water.

### 3.6 Characterization of carbon deposits

In general, carbon deposits can physically cover the catalyst surface and result in the loss of activity. Thus, carbon deposition, as a major catalyst deactivation factor, was investigated in this study. Firstly, the amount of carbon deposits on the spent catalysts was measured by using a TGA. In Figure 7A, the weight loss of the Ni\(_x\)Mg\(_y\)O reached ca. 24 wt%, while the Ni\(_x\)Mg\(_y\)O–Ce exhibited much better performance with less than 1 wt% of weight loss. In addition, Raman spectrum illustrated in Figure 7B shows that the spent Ni\(_x\)Mg\(_y\)O exhibited much stronger integrated intensity of both D band (disordered carbon) and G band (graphite structure) if compared with the spent Ni\(_x\)Mg\(_y\)O–Ce.\(^{56,57}\) In brief, both previous results indicate a dramatic promotion of catalyst capability in anti-carbon formation (Table 5).

In order to figure out the mechanism behind this promotion, the XPS technique was applied to elucidate the

**TABLE 4** Comparison of catalytic performance of different catalysts

| Catalyst                       | T, °C | S/C | GHSV, h\(^{-1}\) | Y\(_{H2}\), mol/molethanol |
|--------------------------------|------|-----|-----------------|--------------------------|
| Pt/CeO\(_2\) (rod)\(^49\)       | 550  | 5.0 | 30 000          | 4.52                     |
| Ni/MgAl\(_2\)O\(_4\)\(^50\)      | 625  | 3.0 | 2700            | 3.87                     |
| LaNi\(_1-x\)Co\(_x\)O\(_3/\)ZrO\(_2\)\(^51\) | 650  | 1.5 | 264 000         | 3.60                     |
| LaNiO\(_3\)\(^52\)              | 700  | 1.5 | 120 000         | 3.90                     |
| Ni/La\(_2\)O\(_3/\)Al\(_2\)O\(_3\)\(^53\) | 700  | 3.0 | 1000            | 3.24                     |
| Ni/Y\(_2\)O\(_3\)\(^54\)        | 650  | 4.2 | 10 000          | 5.25                     |
| Ni\(_x\)Mg\(_y\)O–Ce (this study)| 700  | 3.0 | 200 000         | 4.82                     |

**FIGURE 7** A, TGA profiles of the spent catalysts after 30-hour steam reforming. B, Raman spectra of the spent catalysts. C–D, C 1s spectra of the spent Ni\(_x\)Mg\(_y\)O and Ni\(_x\)Mg\(_y\)O–Ce, respectively (reaction conditions: 700 °C, S/C = 3, GHSV: 200 000 h\(^{-1}\), P = 1 atm) [Colour figure can be viewed at wileyonlinelibrary.com]
nature of carbon species on catalyst surface at the C 1s region (in Figure 7 and Table S3). In the patterns, the main peak and the other two attached shoulders can be classified as follows: 285.0 ± 0.2 eV for graphite structure, 24 285.8 ± 0.2 eV for “defects” or crystalline imperfections associated with disordered carbonaceous materials, 58,59 and 288 to 291 eV for CO32− species on MgO surface. 60 It was observed that the graphite peak intensity of the spent Ni,Mg,O was very high, but its defect peak was relatively low (Figure 7C), while the spent Ni,Mg,O-Ce had a very low intensity of the graphitic peak but higher intensity of the defect peak (Figure 7D). It should be emphasized that graphitic carbon is less reactive and more difficult for gasification. On the other hand, these types of carbon films can encapsulate active metal and cause catalytic activity loss. According to the mechanism of carbon growth, the graphitic forms are mainly located at 26.6°.17 This is in agreement with the findings of previous carbon deposit study. In addition, shoulder peak of metallic Ni, nickel peaks were detected by the XRD. Coincidentally, the Ni2+ ions in the subsurface layers of the Ni,Mg,O solid solution are ca. 17.4 nm. Therefore, the deacceleration of Ni particle growth over the Ni,Mg,O-Ce could also contribute to its durability.

The XRD spectrum of the spent catalyst, in Figure 3C, showed that a unique diffraction peak located at 26.6° was observed on the spent Ni,Mg,O. It indicates existence of significant amount of highly ordered carbon, 62 which is in agreement with the findings of previous carbon deposit study. In addition, shoulder peak of metallic Ni on both spent catalysts positioned at 2θ near 44.1°.17 This indicates that the Ni2+ ions in the subsurface layers of the Ni,Mg,O matrix was reduced after 30-hour reaction. 34 However, the difference is that more metallic nickel peaks were also found at 51.3° and 76.1° for the spent Ni,Mg,O-Ce. In contrast to the previous H2-TPR result, we believe that the surface-covered CeOx nanoparticles hindered hydrogen permeating into the matrix of solid solution and brought down the total reducibility of Ni,Mg,O-Ce. But this surface CeOx also altered the neighbouring nickel electronic property and improved their reducibility. This explained why more metallic nickel peaks were detected by the XRD. Coincidentally, more surface Ni0 sites were also confirmed by XPS.

The surface Ni oxidation states were investigated by using XPS. Both the reduced and spent catalysts were analysed to compare their initial and final states. The Ni 2p spectra and deconvolution details are illustrated in Figure 9 and Tables S2 and S3. The binding energies of Ni0, Ni2+, and Ni4+ in Ni,Mg,O solid solution are ca. 853.0, 854.8, and 856.7 eV. 24 For the reduced catalysts, no Ni0 was observed for all the three catalysts. This is also similar to the XRD analysis results of the freshly reduced catalysts. The reduction for 2 hours at 700°C still could not overcome the bonding forces of Ni-O-MgO sites. For

### Table 5: Raman spectra and key features of different catalysts after peak deconvolution

| Catalysts | Peak Labela | Peak Position, cm⁻¹ | FWHM, cm⁻¹ | L₀, nm |
|-----------|-------------|---------------------|------------|--------|
| Ni,Mg,O  | D (65%)     | 1329                | 115        | 2.7    |
|           | G (35%)     | 1596                | 67         |        |
| Ni,Mg,O-Ce | D (70%)     | 1334                | 51         | 2.1    |
|           | G (30%)     | 1599                | 39         |        |

*aThe values in parentheses represent the percentage area of each peak after deconvolution.

3.7 | Characterization of the spent catalysts

The spent catalysts in this research were also investigated with other characterization methods. The N₂ adsorption-desorption analysis was employed again to test the spent catalysts after 30-hour reaction, as shown in Table 3. Normally, the specific surface area and pore volume of the spent catalysts will decrease compared with those of their fresh state. This could be associated with pore blockage by carbon deposition and surface metal restructure after reforming test. However, the surface area and pore volume of the spent Ni₃Mg₇O catalyst increased, instead. Based on the results of carbon deposit analyses, it was believed that this extraordinary increment was mainly because of the formation of a considerable amount of porous carbon over the catalyst surface. In TEM micrograph Figure 8A,B, the filamentous carbons over the surface of the spent Ni₃Mg₇O were confirmed, while the TEM observation of the spent catalyst Ni₃Mg₇O-Ce did not find any graphited structure.

The sintering of surface nickel particles was determined by manual measurement from TEM images. In Figure 8C,D, both reduced Ni,Mg,O and Ni,Mg,O-Ce catalysts showed very similar particle size distribution with average size of 7.2 and 7.1 nm, respectively. While, comparing both spent catalysts in Figure 8E,F after reaction at 700°C for 30 hours, the spent Ni,Mg,O-Ce showed relatively higher ratio of particles located in both size ranges between 5 to less than 10 and 10 to less than 15 nm, and its average particle size 14.7 nm is also smaller than that of the spent Ni₃Mg₇O at 17.4 nm. Therefore, the deacceleration of Ni particle growth over the Ni₃Mg₇O-Ce could also contribute to its durability.
FIGURE 8  Electron microscopy characterization. TEM images of spent (A) Ni$_x$Mg$_y$O and (B) Ni$_x$Mg$_y$O-Ce after 30-hour reaction (reaction conditions: 700 °C, S/C = 3, GHSV: 200 000 h$^{-1}$, P = 1 atm). Ni particle size distribution of both reduced (C) Ni$_x$Mg$_y$O and (D) Ni$_x$Mg$_y$O-Ce and spent (E) Ni$_x$Mg$_y$O and (F) Ni$_x$Mg$_y$O-Ce after 30-hour reaction [Colour figure can be viewed at wileyonlinelibrary.com]
the spent catalysts, NiₓMgₙO exhibited a substantial attenuation on the intensity of the Ni 2p, compared with NiₓMgₙO–Ce. The reason could be that the surface of the NiₓMgₙO catalyst had severe deposited carbon, which formed a carbon layer and covered the surface Ni ions. Ni⁰ was observed on both the spent NiₓMgₙO and the spent NiₓMgₙO–Ce, which was consistent with the results of XRD analysis. However, in Table S3, the different Ni⁰ and Ni²⁺ surface atomic compositions of both spent catalysts also demonstrated that the chemical environment of surface Ni changed because of the surface-grown CeOₓ. For the spent NiₓMgₙO–Ce, 12.4 wt% of Ni⁰ was on the catalyst surface, while this figure was 19.1 wt% for the spent NiₓMgₙO. This finding was also in agreement with the H₂–TPR result that surface CeOₓ would partially cover nickel ions. However, if we took the total number of Ni sites into account, the spent NiₓMgₙO–Ce (5.38 wt% total Ni on the surface) had more Ni⁰ sites than that of the spent NiₓMgₙO (2.85 wt% total Ni on the surface). This means that more nickel ions had been reduced and formed Ni⁰–CeOₓ over the NiₓMgₙO–Ce. The presence of Ce³⁺ was also confirmed by the Ce 3d spectra as shown in Figure S1.⁶³

the mitigation of carbon deposition, and the extension of catalyst durability. It is found that the promotion of WGSR and the inhibition of methanation played as dominant role in promoting hydrogen yield. In the long-term test at a high GHSV at 200 000 hour⁻¹, the NiₓMgₙO–Ce catalyst showed an outstanding stable high hydrogen yield of 4.82 mol/mol ethanol, which is promising to be used commercially for hydrogen production from SRE.

ACKNOWLEDGEMENTS

The following funding bodies are acknowledged for partially sponsoring this research: National Key R&D Program of China (2017YFB0602602 and 2017YFC0210400) and the Ningbo Bureau of Science and Technology (2012B82011 and 2012B10042).

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4 | CONCLUSIONS

In this research, it was found that the addition of CeOₓ improved the performance of NiₓMgₙO matrix in SRE, which was indicated by the enhanced hydrogen yield,
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**How to cite this article:** Luo X, Hong Y, Zhang H, Shi K, Yang G, Wu T. Highly efficient steam reforming of ethanol (SRE) over CeO2 grown on the nano Ni,MgO matrix: H2 production under a high GHSV condition. *Int J Energy Res.* 2019;43:3823–3836. [https://doi.org/10.1002/er.4549](https://doi.org/10.1002/er.4549)