Highly efficient steam reforming of ethanol (SRE) over CeOx grown on the nano NixMgyO matrix: H2 production under a high GHSV condition

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Highly efficient steam reforming of ethanol (SRE) over CeO_x grown on the nano Ni_xMg_yO matrix: H_2 production under a high GHSV condition

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Abstract

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_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_x was firstly loaded onto a nano-scaled Ni_xMg_yO matrix and subsequently used as the catalyst for hydrogen production via SRE. Morphology of the catalyst materials was characterised by using a series of technologies, whilst H_2-temperature programmed reduction (H_2-TPR), CO-temperature programmed deposition (CO-TPD) and X-ray photoelectron spectroscopy (XPS), etc., 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 - 800 °C. The CeO_x-coated nano Ni_xMg_yO matrix exhibited an outstanding hydrogen yield of 4.82 $mol/mol_{ethanol}$ under a high gas hourly space velocity (GHSV) of 200,000 h^{-1}. It is found that the unique Ni^0-CeO_x structure facilitates the adsorption of CO on the surface and therefore promotes the effective hydrogen production via WGSR. Moreover, this modified Ni_xMg_yO matrix is found to be a more robust and anti-coking nano-catalyst due to reversible switch between Ce^{4+} and Ce^{3+}.

Keywords: Steam reforming of ethanol; hydrogen production; Ni_xMg_yO matrix; CeO_2; water-gas shift reaction

1. INTRODUCTION

The unique features of hydrogen, such as clean, inexhaustible, high conversion efficiency, make it a versatile energy carrier [1]. Currently, fossil fuels account for more than 90% of hydrogen production. The main processes for hydrogen production include natural gas reforming, coal and heavy oil gasification [2, 3], which are associated with formation of a fair amount of CO and SO_x as by-products. Along with the rise of fuel-cell hybrid electric vehicles [4, 5], higher purity hydrogen production from sustainable energy resources becomes particularly attractive in this regard [6].

Bio-ethanol has been increasingly used as a fuel and is considered as a promising alternative fuel for fuel cell due to its high H/C ratio and low cost of production [7]. It has the advantages of eliminating the risks and difficulties associated with the storage and transportation of hydrogen [8-10]. Therefore, hydrogen production from steam reforming of ethanol has been widely studied [8, 11, 12]. 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 products distribution [11, 13].

To date, a suite of active metals (Pt, Rh, Pd, Ni, Cu, Zn, Fe) have been studied extensively as catalysts for SRE [14]. 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 etc [15]. In our previous research [16], the nano-scaled MgO with a high specific surface area was synthesized as the supporting material of a novel Ni_xMg_yO matrix that exhibited a outstanding reforming activity and much better coke resistance ability when compared with the Ni/Al_2O_3 based catalysts and other commercialized catalysts. It is reported that the supporting material, MgO, can facilitate CO_2 adsorption to accelerate the rate of coke gasification [16, 17]. 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 - 900 ℃ [18]. One of the reasons is that carbon deposition could be mitigated at high temperatures [19]. However, moderate temperature (> 600 ℃) will thermodynamically inhibit H_2 formation via WGSR and lead to an excessive amount of CO in the product, which would hinder its further application in fuel cell [20, 21]. Therefore, low temperature SRE (< 400 ℃) is highly attractive and is usually achieved by using various noble metals such as Pt, Rh, Ru, Pd, etc. [11, 13, 22, 23]. 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 improve the reducibility of Ni^{2+} ions [24]. In fact, the spare electrons from Ce^{3+} could migrate to neighbouring Ni^{2+} ions and increase the reducibility of the subsurface Ni^{2+} ions [25]. This activation of nickel sites may improve hydrogen production via the acceleration of ions exchange between CO and H_2O. On the other hand, CeO_2 can accelerate water dissociation to form OH^- groups, which are essential for the hydrogen production from C_xH and C_yO_zH [26, 27].

To develop a robust catalyst for the in-situ hydrogen production in fuel cells, in this study, nano CeO_x clusters were grown over the novel Ni_xMg_yO matrix to introduce new interactions between CeO_x clusters and the restrained nickel ions inside the subsurface MgO matrix. The effect of this Ni^0-CeO_x over WGSR was investigated under moderate temperature (> 600 ℃). The overall catalytic performance in SRE was also studied under a high GHSV condition with a focus on hydrogen yield and anti-carbon formation ability.

2. EXPERIMENTAL

2.1 Preparation of catalysts

All chemicals used in this research are of analytical (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). Two types of catalysts, i.e., NixMgyO, NixMgyO-Ce, were prepared following the procedures described elsewhere [16]. 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 h [28]. The treated slurry was subsequently filtered without washing, dried at 120 °C for 24 h, and calcinated at 700 °C for 6 h. 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 Ni_xMg_yO 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 Barett-Joyner-Halenda (BJH) procedure described elsewhere [29], the specific surface area, pore volume and micropore volume of both fresh and spent catalysts were characterised by using a Micrometrics ASAP-2020. The measurements were performed at -196 °C, after the degas process at 300 °C for 5 h.

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 s.

The reducibility of nickel species on the fresh catalysts was studied via H_2-temperature programmed reduction (H_2-TPR) (Finetec, Finesorb 3010D) following the process detailed elsewhere [16]. In each test, approximately 30 mg of the catalyst was pre-treated at 300 °C in argon (99.999%) and then heated from room temperature to 1000 ℃ at a heating rate of 5 ℃/min under a specific atmosphere (10 vol% H_2 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 H_2 at 700 ℃ for 2 h. The inflow gas was then switched to pure argon (99.999%) to purge off the residual H_2. Meanwhile, the bed temperature was decreased to 300 ℃ and kept isothermal for 1 h. The CO adsorption was conducted at room temperature for 30 min, 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 ℃ at a heat rate of 5 ℃/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 ℃ for 20 min, and then heated to 1000 ℃ at a heating rate of 10 ℃/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 3 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 Axis Ultradld 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 analyzed to find out the transformation of oxidation state of the surface metals.

The texture of the catalysts and the deposited carbon was observed using a transmission electron microscope (TEM, JEOL JEM-2100F). For the sample preparation, the catalyst powder was dispersed in ethanol with 3 min 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 Fig. 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 ℃ for 2 h under 25 vol% H_2 in N_2 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 were 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 ℃) 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, I.D. = 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 off-line by using a Gas Chromatograph (SHIMADZU, GC-2014). For each catalyst, its catalytic activity was tested at four different temperature levels, i.e., 500, 600, 700 and 800 ℃. The composition of gas outflow was analysed 2 h after temperature of the catalyst bed had become stable. For the durability test, catalytic reforming was carried out at 700 ℃ and lasted for 30 h. 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):

$$H_2\text{ yield (mol/mol}_{\text{ethanol}}) = \frac{mole\ of\ produced\ hydrogen}{mole\ of\ input\ ethanol \times 6} \tag{1}$$

The conversion of ethanol ($X_{ethanol}$) was calculated only based on the production of CO_2, CH_4 and CO. Other products, such as ethylene, acetaldehyde and acetylene, were neglected due to their extremely low mole fractions in the gas product [30].

$$X_{ethanol}\,(\%) = \frac{carbon\ mole\ of\ total\ products}{mole\ of\ input\ ethanol \times 2} \cdot 100\% \qquad (2)$$

The yield of carbonaceous gases, such as CO_2, CO and CH_4, was calculated by:

$$\text{Carbonaceous gas yield (mol/mol}_{\text{ethanol}}) = \frac{\text{mole of produced carbonaceous gas}}{mole\ of\ input\ ethanol \times 2} \qquad (3)$$

3. RESULTS AND DISCUSSION

3.1 N_2 adsorption-desorption analysis

Structural features of the catalysts were characterised following the BET method, the results of which are illustrated in Table 3. It is clear that the fresh catalyst Ni_xMg_yO-Ce showed a very similar surface property to the Ni_xMg_yO 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 Fig. 2 [16].

3.2 XRD analysis

Fig. 3 (A) 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 Ni_xMg_yO matrix is actually a rocksalt-structure solid solution due to the similar ionic radius and the same valence number of Ni^{2+} and Mg^{2+} ions [16, 31]. For the fresh Ni_xMg_yO-Ce, fluorite phase of CeO_2 was observed with weak intensity, which indicates small CeO_2 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 rocksalt 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 SRE [24].

3.3 Characteristics of Ni species

The H_2-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 Fig. 4 (A). For the Ni_xMg_yO catalyst, the main peak (at 889 °C) was attributed to the reduction of Ni^{2+} ions dissolved inside the MgO lattice to form Ni_xMg_yO solid solution [34]. The broad shoulder peak at 630 °C or above was confirmed as the reduction of Ni^{2+} ions at sublayers in previous work [16].

For the Ni_xMg_yO-Ce, it is obvious that the total reducibility of primary nickel specie (around 884 °C) decreased after the doping with promoters, which suggests that surface isolated CeO_2 could consume surface hydrogen gas and hinder hydrogen from penetrating into the matrix of solid solution for Ni^{2+} reduction [35]. The broad shoulder peak near 730 °C could also be explained as the reduction of Ni^{2+} at sublayers [24, 34], which was similar with the situation of the shoulder peak of the Ni_xMg_yO at 630 °C. These broad shoulder peaks could also be attributed to the reduction of CeO_2 particles dispersed on the surface [36, 37]. Moreover, there is a noticeable broad peak at the low temperature region of 300-550 °C. The existence of this reduction peak could be explained by two reasons. The first reason is the direct reduction of surface CeO_2 particles. At this temperature, CeO_2 particles can be reduced from Ce^{4+} to Ce^{3+} by H_2 [21, 36]. 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 [24, 25, 38]. 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 [39, 40]. 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 h.

As shown in Fig. 3 (B), no peaks for the reduced Ni^0 were observed in the XRD pattern of the reduced Ni_xMg_yO. However, in the TPR pattern of the Ni_xMg_yO, low intensity humps in the temperature range of 300-550 °C were observed and it could be only ascribed to the existence of a small amount of Ni^{2+} ions over the surface [16]. The reason for such could be that Ni^0 particles were highly dispersed on the internal surface of the support or the formation of small size Ni^0 crystals (< 5 nm), which cannot be detected by XRD analysis [41, 42]. For the Ni_xMg_yO-Ce, it was different from the Ni_xMg_yO catalyst that Ni (220) peak was found near 76.1°. Combined with the XPS results (shown in Fig. S1), in which the reduction of CeO_2 was detected, it could be speculated that surface CeO_2 is reduced under reducing atmosphere and form vacancies. These vacancies make the reduced CeO_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^0-CeO_x structure.

3.4 CO-TPD analysis

It is reported that the site for CO adsorption is Ni crystal but not the MgO support [43]. In this study, CO-temperature programmed desorption was carried out to find out the interactions between Ni sites and CO molecules. In Fig. 4 (B), the desorption peaks observed over the Ni_xMg_yO 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) [38, 44]. The second peak group, located in a higher temperature region (200-350 °C), could be attributed to more strongly bonded CO molecules [38]. The broader peaks, desorbed at temperatures above 400 °C, are associated with the CO dissociative adsorption over the stepped nickel surface (β site) [43]. Moreover, the board peaks above 400 °C could also be attributed to the formation of CO_2 due to oxidation of the adsorbed CO by the subsurface metal oxides or the product from WGSR of CO and surface hydroxyl groups [43, 45, 46]. Compared 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_xMg_yO-Ce showed much higher intensity peak above 400 °C, it confirmed the addition of CeO_2 facilitates the adsorption of CO at higher temperature. Moreover, higher capability of CO adsorption promotes the WGSR and results in a higher H_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 mole of ethanol can produce 6 moles of H_2. However, some hydrogen molecules might participate in methanation reaction (the reverse of R12), and WGSR (R9) might be inhibited at a certain extend due to high temperature condition. As shown in Fig. 5 (A), the Ni_xMg_yO catalyst showed relatively low selectivity in hydrogen yield. At lower temperatures, for instance, 500 °C, the Ni_xMg_yO catalyst only resulted in a H_2 yield of 0.75 $mol/mol_{ethanol}$, while the Ni_xMg_yO-Ce catalyst had considerably higher H_2 yields of 2.47 $mol/mol_{ethanol}$. At higher temperatures, such as 600, 700 and 800 °C, the initial H_2 yields of the modified catalyst were all above 4.70 $mol/mol_{ethanol}$, while the highest yield for the Ni_xMg_yO catalyst was only 3.34 $mol/mol_{ethanol}$ 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 Fig. 5 (B)) that the Ni_xMg_yO catalyst showed a much lower ethanol conversion of 21.5% at 500 °C if compare to Ni_xMg_yO-Ce, which had a more then double conversion of 49.8%. This result is consistent with their hydrogen yield. On the contrary, the ethanol conversion of the Ni_xMg_yO catalyst at temperatures above 600 °C was 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 h and the results are shown in Fig. 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 (Ni^{2+}) and dispersed inside sublayers of the Ni_xMg_yO matrix, which were not reduced to Ni^0 during the hydrogen reduction process. However, these Ni^{2+} ions were slowly reduced during the reforming process due to the higher H_2 concentration in gas phase. Therefore, more newly reduced Ni^0 sites formed when the SRE process proceeded, which resulted in the formation of more active sites and subsequently led to higher H_2 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 Fig. 3 (B) and (C). It was found that the XRD spectrums of the reduced catalysts showed no Ni^0 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 Ni_xMg_yO-Ce catalyst showed a high efficiency in hydrogen production with a yield of 4.82 $mol/mol_{ethanol}$, which was achieved an extremely high GHSV (200,000 h^{-1}) applied in this study. In Table 4, the Ni_xMg_yO-Ce catalyst is also compared with many other nickel-based catalysts from recent literatures [49-54]. It is noteworthy that the Ni/Y_2O_3 catalyst was the only catalyst, which showed higher hydrogen yield at 5.25 $mol/mol_{ethanol}$, while its space velocity was only one-twentieth of what was applied to Ni_xMg_yO-Ce in this study.

3.5.3 Evolution of gas yields

From Fig. 6, it can be observed that the Ni_xMg_yO had higher ethanol conversion but lower hydrogen production. The reason behind this was further investigated by comparing the carbonaceous gases yields. For the modified catalyst, the Ni_xMg_yO-Ce had different tendency in the yield of gas products. It showed lower methane yield, which suggested 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 H_2. On the other hand, the surface carbon and CO were also favoured to be oxidized by the surface oxygen from CeO_2 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 Ni_xMg_yO-Ce catalyst also had higher CO_2 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 oxidised to CO_2 by the vicinal CeO_x particles. Then the reduced CeO_x captures oxygen from the dissociation of water to production H_2. 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 H_2 and CO_2 from C_xH and C_yO_xH 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 results 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 Fig. 7 (A), the weight loss of the Ni_xMg_yO reached ca. 24 wt%, while the Ni_xMg_yO-Ce exhibited much better performance with less than 1 wt% of weight loss. In addition, raman spectrum illustrated in Fig. 7 (B) shows that the spent Ni_xMg_yO exhibited much stronger integrated intensity of both D band (disordered carbon) and G band (graphite structure) if compared with the spent Ni_xMg_yO-Ce [56, 57]. In brief, both previous results indicate a dramatic promotion of catalyst capability in anti-carbon formation.

In order to figure out the mechanism behind this promotion, the XPS technique was applied to elucidate the nature of carbon species on catalysts surface at the C 1s region (in Fig. 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]; 288-291 eV for CO_3^{2-} species on MgO surface [60]. It was observed that the graphite peak intensity of the spent Ni_xMg_yO was very high but its “defects” peak was relatively low (Fig. 7 (C)), while the spent Ni_xMg_yO-Ce had a very low intensity of the graphite peak but higher intensity of the “defects” peak (Fig. 7 (D)). It should be emphasized that graphitic carbon is less reactive and more difficulty 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 is transformed from the surface accumulated carbon precursors at high temperature (> 600 °C) [47]. Thus, it can be speculated that the Ni_xMg_yO-Ce catalyst increased the gasification rate of carbon precursors lead to much less formation of ordered graphitic carbon. In fact, surface CeO_x has a property of reversible shift of oxidation state ($Ce^{4+} \rightleftharpoons Ce^{3+}$). The surface cerium oxide can act as a source of oxygen supply as well as sink for oxygen capture [61]. Thus, the grown CeO_x can provide highly mobile oxygen atoms for deposited carbon removal.

3.7 Characterization of the spent catalysts

The spent catalysts in this research were also investigated with other characterization methods. The N_2 adsorption-desorption analysis was employed again to test the spent catalysts after 30 h 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 pores blockage by carbon deposition and surface metal restructure after reforming test. However, the surface area and pore volume of the spent Ni_xMg_yO catalyst increased, instead. Based on the results of carbon deposits analyses, it was believed that this extraordinary increment was mainly due to the formation of a considerable amount of porous carbon over the catalyst surface. In TEM micrograph Fig. 8 (A) and (B), the filamentous carbons over the surface of the spent Ni_xMg_yO were confirmed, while the TEM observation of the spent catalyst Ni_xMg_yO-Ce did not find any graphited structure.

The sintering of surface nickel particles was determined by manual measurement from TEM images. In Fig. 8 (C) and (D), both reduced Ni_xMg_yO and Ni_xMg_yO-Ce catalysts showed very similar particle size distribution with average size of 7.2 and 7.1 nm, respectively. While, compared both spent catalysts in Fig. 8 (E) and (F) after reaction at 700 °C for 30 h, the spent Ni_xMg_yO-Ce showed relatively higher ratio of particles located in both size ranges between 5 to <10 nm and 10 to <15 nm, as well as its average particle size 14.7 nm is also smaller than that of the spent Ni_xMg_yO at 17.4 nm. Therefore, the deceleration of Ni particle growth over the Ni_xMg_yO-Ce could also contribute to its durability.

The XRD spectrum of the spent catalyst, in Fig. 3 (C), showed a unique diffraction peak located at 26.6° was observed on the spent Ni_xMg_yO. It indicates existence of significant amount of highly ordered carbon [62], which is in agreement with the findings of previous carbon deposits study. In addition, shoulder peak of metallic Ni on both spent catalysts positioned at 2θ near 44.1° [17]. This indicates the Ni^{2+} ions in the sub-surface layers of the Ni_xMg_yO matrix was reduced after 30 h reaction [34]. However, the difference is more metallic nickel peaks were also found at 51.3° and 76.1° for the spent Ni_xMg_yO-Ce. Contrasted the previous H_2-TPR result, we believe that the surface covered CeO_x nanoparticles hindered hydrogen permeating into the matrix of solid solution and brought down the total reducibility of Ni_xMg_yO-Ce. But this surface CeO_x also alter the neighbouring nickel electronic property and improved their reducibility. This explained why more metallic nickel peaks were detected by the XRD. Coincidentally, more surface Ni^0 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 Fig. 9, Table S2 and S3. The binding energies of Ni^0, Ni^{2+} and Ni^{3+} in Ni_xMg_yO solid solution are ca. 853.0 eV, 854.8 eV and 856.7 eV [24]. For the reduced catalysts, no Ni^0 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 h at 700 ℃ still could not overcome the bonding forces of Ni-O-MgO sites. For the spent catalysts, Ni_xMg_yO exhibited a substantial attenuation on the intensity of the Ni 2p, compared with Ni_xMg_yO-Ce. The reason could be that the surface of the Ni_xMg_yO catalyst had severe deposited carbon, which formed a carbon layer and covered the surface Ni ions. Ni^0 was observed on both the spent Ni_xMg_yO and the spent Ni_xMg_yO-Ce, which was consistent with the results of XRD analysis. However, in Table S3, the different Ni^0 and Ni^{2+} surface atomic compositions of both spent catalysts also demonstrated that the chemical environment of surface Ni changed due to the surface grown CeO_x. For the spent Ni_xMg_yO-Ce, 12.4 wt% of Ni^0 was on the catalyst surface, while this figure was 19.1 wt% for the spent Ni_xMg_yO. This finding was also in agreement with the H_2-TPR result that surface CeO_x would partially cover nickel ions. However, if took the total number of Ni sites into account, the spent Ni_xMg_yO-Ce (5.38 wt% total Ni on the surface) had more Ni^0 sites than that of the spent Ni_xMg_yO (2.85 wt% total Ni on the surface). This means more nickel ions had been reduced and formed Ni^0-CeO_x over the Ni_xMg_yO-Ce. The presence of Ce^{3+} was also confirmed by the Ce 3d spectra as shown in Fig. S1 [63].

4. CONCLUSIONS

In this research, it was found that the addition of CeO_x improved the performance of Ni_xMg_yO matrix in SRE, which is indicated by the enhanced hydrogen yield, 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 h^{-1}, the Ni_xMg_yO-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.

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Tables

Table 1 Primary and side reactions of steam reforming of ethanol.

No.	Reaction name	Reaction equation
R1	Steam reforming of ethanol	$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$
R2	Decomposition of ethanol	$C_2H_5OH \rightarrow CH_4 + CO + H_2$
R3	Ethanol dehydrogenation to acetaldehyde	$C_2H_5OH \rightarrow C_2H_4O + H_2$
R4	Ethanol dehydration to ethylene	$C_2H_5OH \rightarrow C_2H_4 + H_2O$
R5	Steam reforming of acetaldehyde	$C_2H_4O + 3H_2O \rightarrow 2CO_2 + 5H_2$
R6	Decomposition of acetaldehyde	$C_2H_4O \rightarrow CO + CH_4$
R7	Steam reforming of ethylene	$C_2H_4 + 4H_2O \rightarrow 2CO_2 + 6H_2$
R8	Decomposition of ethylene	$C_2H_4 \rightarrow C + CH_4$
R9	Water-gas shift reaction	$CO + H_2O \rightleftharpoons CO_2 + H_2$
R10	Steam reforming of methane	$CH_4 + H_2O \rightleftharpoons CO + 3H_2$
R11	CO disproportionation reaction	$2CO \rightleftharpoons CO_2 + C$ (coke)
R12	Decomposition of methane	$CH_4 \rightleftharpoons 2H_2 + C$ (coke)
R13	Carbon gasification by steam	$C + H_2O \rightleftharpoons CO + H_2$

Table 2 Elemental analysis results of fresh catalysts.

Catalyst name	Theoretical element mass composition		Measured element mass composition[a]	
	Ni	Promoter element (Ce)	Ni	Promoter element (Ce)
Ni_xMg_yO	10%	N/A	8.4%	N/A
Ni_xMg_yO-Ce	10%	3%	8.3%	2.3%

[a] Measured by using ICP-AES.

Table 3 Structural characteristics of both fresh and spent catalysts.

catalysts	Surface area (m^2/g)	Pore volume (cm^3/g)	Micropore volume (cm^3/g)	Pore size (nm)
Fresh Ni_xMg_yO	56	0.28	0.0059	20
Used Ni_xMg_yO	138	0.47	0.0090	14
Fresh Ni_xMg_yO-Ce	52	0.29	0.0045	22
Used Ni_xMg_yO-Ce	37	0.12	0.0024	13

Table 4 Comparison of catalytic performance of different catalysts.

Catalyst	T (℃)	S/C	GHSV (h^{-1})	Y_{H2} (mol/$mol_{ethanol}$)
Pt/CeO_2 (rod) [49]	550	5.0	30,000	4.52
Ni/$MgAl_2O_4$ [50]	625	3.0	2,700	3.87
$LaNi_{1-x}Co_xO_3$/ZrO_2 [51]	650	1.5	264,000	3.60
$LaNiO_3$ [52]	700	1.5	120,000	3.90
Ni/La_2O_3-αAl_2O_3 [53]	700	3.0	1,000	3.24
Ni/Y_2O_3 [54]	650	4.2	10,000	5.25
Ni_xMg_yO-Ce (This study)	700	3.0	200,000	4.82

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

Catalysts	Peak label[a]	Peak position (cm^{-1})	FWHM (cm^{-1})	L_a (nm)
Ni_xMg_yO	D (65%)	1329	115	2.7
	G (35%)	1596	67	
Ni_xMg_yO-Ce	D (70%)	1334	51	2.1
	G (30%)	1599	39	

[a] The values in parentheses represent the percentage area of each peak after deconvolution.