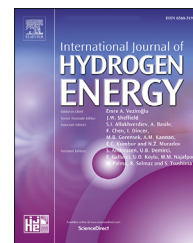


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Synthesis of NiO/MgO/ZrO₂ catalyst for syngas production from partial oxidation and dry reforming of biogas

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HIGHLIGHTS

- Surface modification of NiO/ZrO₂/MgO by carbon derived from urea was studied.
- NiO/ZrO₂/MgO catalyst was applied for partial oxidation and dry reforming of biogas.
- H₂/CO ratio ca. 2 could be obtained using 30%NiO/ZrO₂/20MgO catalyst.
- High stability was obtained for the 30%NiO/ZrO₂/20MgO.

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ABSTRACT

This work focuses on a facile NiO/MgO/ZrO₂ synthesis protocol for syngas production via partial oxidation and dry reforming of biogas. Herein, performance of the developed catalysts with different amounts of MgO (0–40 %wt. of support) and NiO (10–50 %wt.) on %CH₄ conversion, %CO₂ conversion, H₂/CO ratio, and carbon formation are studied. The results reveal the presence of monoclinic ZrO₂ and tetragonal ZrO₂ phases with 50%NiO/ZrO₂ catalyst synthesized by surface modification technique using carbon derived from urea. Addition of MgO in the catalyst shows ability to stabilize tetragonal ZrO₂ phase as well as

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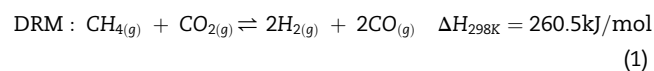
enhance basic surface of the catalyst. These properties render the adsorption of CO₂ molecules on the surface, which subsequently are reduced by carbon, leading to CO production. Appropriated amount of NiO and MgO, which is 30 %wt. NiO and 20 %wt. MgO (relative to ZrO₂) can produce syngas having quality (H₂/CO molar ratio) of ca. 2.

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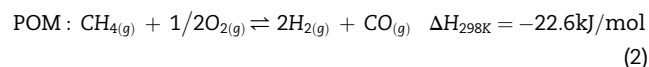
Introduction

Biogas consists mainly of 60–65% methane (CH₄), 30–35% carbon dioxide (CO₂), 1% nitrogen (N₂), and trace amount of H₂S, H₂, and water [1]. At present, converting its main components, CH₄ and CO₂, into synthetic gas (syngas), which can be used to produce fuels and value-added chemicals, is attracting much interest worldwide [2].

The two main components of the biogas, CH₄ and CO₂, can be reformed through the process known as dry reforming of methane (DRM) as presented in Eq. (1) [3]:



By using metal oxide as an oxygen carrier in the process, partial oxidation of methane (POM) can also take place as shown by Eq. (2) [3]:



Ni-based catalysts are widely used in the DRM process due to their high activity towards reforming reaction, availability, and low cost. However, the ease to deactivate due to carbon deposition and metal sintering is a drawback of the catalysts. Attempts to overcome this drawback have been made through, for example, the use of different support materials [4–6], synthesizing via different techniques [1–3,8–10], addition of a second metal [7,11–13], etc. Of these, reports suggested that small particle size of active phase and acid-base property of the surface are two main factors that affect DRM reaction performance and carbon deposition [14–16]. Different catalyst preparation techniques have been employed to improve such properties to enhance the DRM performances [3,10,11,16,17]. Asencios et al. [3] synthesized NiO/MgO/ZrO₂ using a single step polymerization method and tested for the reforming of biogas with the presence of air (CH₄/CO₂/O₂ = 1.5/1/0.25 M ratio) at 750 °C. The results showed that the NiO/MgO/ZrO₂ containing 20 %wt. nickel and 20 %mol MgO relative ZrO₂ provided the best performance on producing H₂/CO of 1.1 with 60% CH₄ conversion and 70% CO₂ conversion. Zanganeh et al. [16] investigated the effect of NiO and MgO contents in Ni–Mg–ZrO₂ catalysts prepared by co-precipitation technique on the DRM performance. Their results revealed that increasing Ni content led to a negative effect on carbon resistance due to the lower of solid solution Mg–ZrO₂ content and larger Ni particle size, which resulted in the formation of carbon deposition. A synergistic effect

between good Ni dispersion and basicity of support surface was also suggested to affect carbon formation and the DRM performance. In their study, the Ni_{0.03}Mg_{0.97}O catalyst showed the best performance on carbon resistance. Liu et al. [8] investigated the use of core-shell catalyst Ni–ZrO₂@SiO₂ (zirconia-modified nickel nanoparticle is a core and microporous silica is a shell) synthesized via a one-pot facile technology for the DRM. The developed catalyst showed significant improvements on coke resistance and particle sintering as well as high stability over 240 h of reaction time and no carbon formation was observed under a harsh reaction temperature at 800 °C. Huang et al. [10] synthesized mesoporous MgO–ZrO₂ supported nickel catalysts for the DRM reaction using surfactant assisted route and impregnation method. Triblock copolymer, P123 (PEO–PPO–PEO), was used during precipitation of MgO–ZrO₂ for the formation of mesoporous structure. Nickel was subsequently loaded on the support by impregnation. Their results showed that the catalyst with 10 %wt. Ni content provided high CH₄ and CO₂ conversion ca. 85% with 90% H₂ and CO selectivity at reaction temperature of 700 °C. Carbon deposition was observed to be minimized at 19.9%. Yusuf et al. [17] studied the effect of Ni/Al₂O₃–MgO preparation method on dry reforming of methane. Two different routes, co-precipitation (one-step method) and co-precipitation followed by Ni impregnation (two-step method), were investigated. Their results showed that the catalyst prepared by the two-step method provided better performances, in terms of CH₄ conversion, CO₂ conversion, H₂/CO ratio, and stability, than the one-step method. The authors claimed that lower performances observed with the one-step method is due to most of the active Ni metal was encapsulated in the lattice of Al₂O₃–MgO while some amount interacted with Mg forming MgNiO₄.

As seen from the literatures, methods to synthesize catalyst affect performances of the catalyst for the DRM reaction [3,10,11,16,17]. Although many techniques are successfully developed to produce efficient catalyst for syngas production via DRM, some of those are likely complicated and do not facilitate for deploying in large-scale production. In this work, we aim to develop a facile method to synthesize NiO/MgO/ZrO₂ catalyst of which it is enabled to facilitate large-scale production for syngas production via partial oxidation and dry reforming of biogas. Surface modification technique using carbon derived from urea is developed for catalyst synthesis. Performances of the developed catalyst containing different amounts of MgO (0–40 %wt. of support) and NiO (10–50 %wt.) are studied in terms of %CH₄ conversion, %CO₂ conversion, carbon formation, and syngas quality (H₂/CO molar ratio).

Materials & methods

Catalyst preparation

Synthesis of NiO/ZrO₂/MgO catalysts via surface modification technique, containing different amounts of MgO (0–40 %wt. of support) and NiO (10–50 %wt) on support ZrO₂, was carried out by mixing ground particles of (Ni(NO₃)₂·6H₂O), zirconyl nitrate (N₂O₇Zr), and urea (CH₄N₂O) at designed amounts. The mixed solids were heated to 500 °C under N₂ atmosphere and held for 2 h followed by ramping to 800 °C and held for 2.5 h to convert urea into carbon. Then, the obtained powder solids were calcined under dry air at 800 °C for 3 h to remove carbon. The samples synthesized by this method are designated by x% NiO/ZrO₂/yMgO-Sm, where x is amount of NiO (%wt.) loaded on the support ZrO₂–MgO and y is amount of MgO (%wt.) relative to ZrO₂.

The NiO/ZrO₂ catalyst synthesized by sol-gel method as reported by Hao et al. [18] was prepared for performance comparison purpose. Firstly, nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O) solution concentration of 0.1 M was gradually added to a 0.18 M-zirconyl nitrate (N₂O₇Zr) solution having pH of 7.5 (using 25 %wt. ammonia to adjust pH of the solution). After well mixing, the solution was adjusted to pH of 9 by dosing with 25 %wt. ammonia solution. Then, the mixture was left at room temperature for 4 h to allow gel forming before washing and rinsing by DI-water and ethanol, respectively. The obtained paste was dried at 110 °C in an oven for 12 h followed by calcination at 650 °C for 4 h (heating rate = 10 °C/min). The samples synthesized by sol-gel method are represented as x%NiO/ZrO₂/yMgO-Sg, where x is amount of NiO (%wt.) loaded on the support ZrO₂–MgO and y is amount of MgO (%wt.) relative to ZrO₂.

Catalyst characterization

Phase composition and crystallinity of the synthesized catalysts were determined by X-ray powder diffraction technique (XRD) in the 2θ range of 10–70° using D8 Advance X-ray diffractometer (Bruker AXS) equipped with a focus Cu Kα x-ray source. All measurements were carried out using a step of 3422, scan speed of 0.500 s/step and wavelength of 1.54 nm N₂ adsorption/desorption experiments were carried out to determine surface area, pore size, and pore volume of the samples. Each measurement was conducted at 77 K by Micromeritics Chemisorp 2750. The Brunauer-Emmett-Teller (BET) method was applied to calculate surface area while the Barret Joyner-Halender (BJH) method was applied to determine pore sizes and pore volumes of the samples. Gas-solid interaction and CH₄ decomposition rate of the catalyst were investigated using CH₄ temperature-programmed surface

reaction technique, (CH₄-TPSR). The investigation was conducted in a fixed-bed reactor by feeding 15 %vol. CH₄ gas (balanced with argon) to make a total flow rate 40 ml/min. Temperature was ramping from room temperature to 850 °C with the heating rate of 5 °C/min. Surface property and elemental distribution were examined by HORIBA scanning electron microscope couple with an energy dispersive spectroscope, (SEM-EDX), which were operated at 15 kV and working distance of 10.2 mm. Temperature-programmed oxidation (TPO) was used to evaluate type and amount of carbon deposit on the catalyst. The experiment was conducted by feeding O₂ of 2 %vol. (Ar balanced) through a fixed-bed reactor for temperature ranging from room temperature to 850 °C using a heating rate of 5 °C/min. The structure of carbon deposits was examined by Raman Spectroscopy, collected by LabRAM HR Evolution using an argon laser at 532 nm. Morphologies of carbon on the spent catalyst were also investigated using a JEM-2100 Plus transmission electron microscope (TEM), all samples were dispersed in ethanol by an ultrasonic sonicator and placed in a carbon film coated copper grid before analysis.

Catalytic reaction test

Catalytic reaction was performed in a fixed-bed reactor system. The catalyst was placed inside a tubular quartz reactor (inner diameter of 9 mm). Simulated biogas, composing of CH₄ 60 %vol. and CO₂ 40 %vol., was fed to the reactor with Ar as a carrier gas at a fixed gas hourly space velocity (GHSV) of 2516 L/g_{cat} · h. The reactor was heated to the desired temperature of 800 °C at atmospheric pressure using an electrical furnace.

Conversions of CH₄ and CO₂ were calculated as follows [18]:

$$\text{CH}_4 \text{ conversion (\%)} = \frac{(\text{moles of CH}_{4,\text{in}} - \text{moles of CH}_{4,\text{out}})}{\text{moles of CH}_{4,\text{in}}} \times 100 \quad (3)$$

$$\text{CO}_2 \text{ conversion (\%)} = \frac{(\text{moles of CO}_{2,\text{in}} - \text{moles of CO}_{2,\text{out}})}{\text{moles of CO}_{2,\text{in}}} \times 100 \quad (4)$$

H₂ and CO selectivity were calculated as [18]:

$$\text{H}_2 \text{ selectivity (\%)} = \frac{\text{moles of H}_2 \text{ produced}}{2 \times (\text{moles of CH}_{4,\text{in}} - \text{moles of CH}_{4,\text{out}})} \times 100 \quad (5)$$

$$\text{CO selectivity (\%)} = \frac{\text{moles of CO produced}}{(\text{moles of CH}_{4,\text{in}} + \text{moles of CO}_{2,\text{in}}) - (\text{moles of CH}_{4,\text{out}} + \text{moles of CO}_{2,\text{out}})} \times 100 \quad (6)$$

Results and discussion

Effect of synthesis method

In this work we compared the performance of our facile method with sol-gel method since it was reported that the catalyst synthesized by sol-gel method showed high performance of reforming reaction [18].

XRD patterns of 50%NiO/ZrO₂ catalyst synthesized by two different methods, surface modification technique (50% NiO–ZrO₂-Sm) versus sol-gel method (50%NiO–ZrO₂-Sg) are shown in Fig. 1. Tetragonal ZrO₂ phase is observed at diffraction peaks $2\theta = 30.3, 36.5, 50.9$ and 60.5° for catalyst prepared by either sol-gel or surface modification technique. However, monoclinic ZrO₂ phase is observed with the 50% NiO/ZrO₂-Sm as revealed by the diffraction peak at $2\theta = 28.3$ and 31.5° [9]. The presence of monoclinic ZrO₂ in the 50%NiO/ZrO₂-Sm indicates an insufficient heat treatment of the sample to form tetragonal structure [19]. NiO representative peaks at $2\theta = 37.4, 43.5$ and 63.2° [20,21] are observed with both catalysts; however, the intensity of the 50%NiO/ZrO₂-Sg is greater than that of the 50%NiO/ZrO₂-Sm. Calculation of NiO crystallite size by Scherrer equation reveals that the 50%NiO/ZrO₂-Sg has smaller NiO crystallite size, 14.7 nm, than that of the 50%NiO/ZrO₂-Sm, 16.7 nm. Small particle size of NiO observed with the 50%NiO/ZrO₂-Sg implies greater dispersion of NiO on the support [9]. The results of N₂ adsorption/desorption isotherm (Fig. S1) reveals that BET surface area and pore volume of the 50%NiO/ZrO₂-Sm are much smaller than that of the 50%NiO/ZrO₂-Sg (Table 1). Such larger surface area

Table 1 – Physical properties and syngas production performances of the 50%NiO/ZrO₂-Sg and the 50% NiOZrO₂-Sm.

Catalysts	50%NiO/ZrO ₂ -Sg	50%NiO/ZrO ₂ -Sm
BET surface area (m ² /g)	26.7	3.59
Pore size (nm)	21.92	48.39
Pore volume (cm ³ /g)	0.16	0.04
CH ₄ conversion (%)	97	97
CO ₂ conversion (%)	100	100
H ₂ /CO	1.9	1.9

and pore volume are a result of the formation of networking particles obtained from sol-gel method. On the other hand, the addition of urea as a carbon source on solid surface results in an enhancement of pore size as observed with the 50%NiO/ZrO₂-Sm.

Both catalysts were tested in terms of CH₄ conversion, CO₂ conversion, and H₂/CO ratio. The results in Table 1 show that CH₄ conversions of both catalysts are similar, which is ca. 97%, whereas a complete CO₂ conversion is observed with both catalysts. There are two gaseous products observed in the product stream: H₂ and CO as demonstrated in Fig. S2. Similar amount of the two gaseous products as well as H₂ selectivity and CO selectivity are obtained from both catalysts for a period of reaction time. This results in similar value of syngas quality (H₂/CO) of ca. 1.9 for both catalysts (Table 1).

Other performances of the developed catalysts were examined in terms of the ability to oxidize CH₄ by NiO via partial oxidation and carbon formation during the reaction proceed. Temperature-programmed surface reaction with

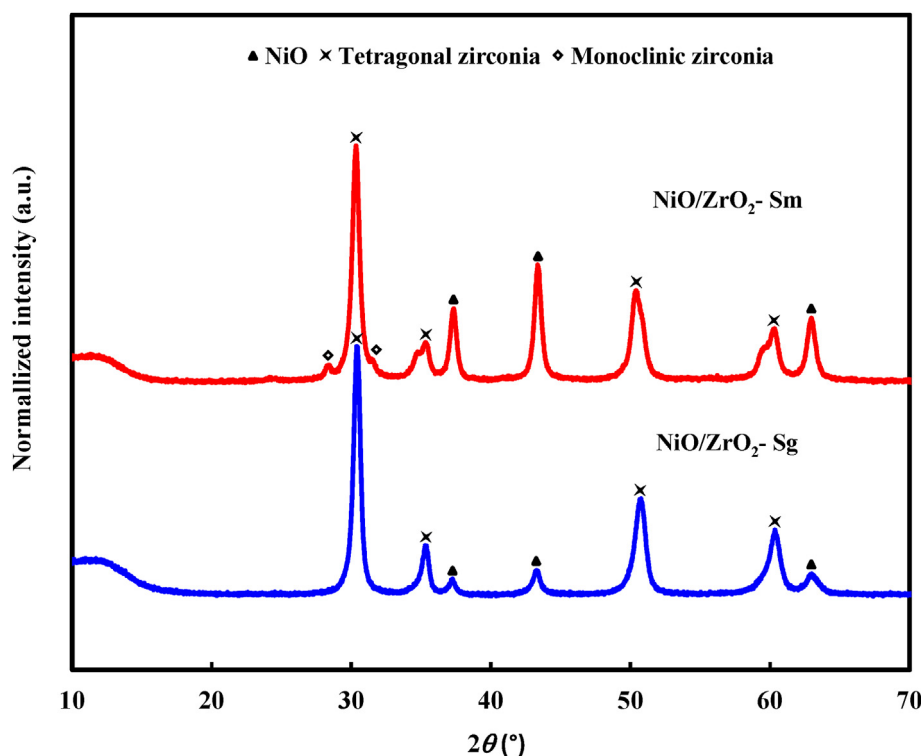


Fig. 1 – XRD pattern of 50%NiO/ZrO₂ catalysts synthesized by surface modification technique, 50%NiO/ZrO₂-Sm, and Sol-gel method, 50%NiO/ZrO₂-Sg.

methane was conducted to investigate gas-solid interaction and CH_4 decomposition. For the 50%NiO/ZrO₂-Sg (Fig. 2(a)), NiO is reduced by CH_4 at temperature ca. 500 °C as CH_4 gradually drops while H_2 and CO are produced according to Eq. (7). It is noteworthy that a small amount of CO_2 is produced during partial oxidation reaction; this could be a result of reversed Boudouard reaction (Eq. (8)), which reflects that methane decomposition (Eq. (9)) also occurs at this temperature. At temperatures higher than 600 °C, only H_2 is produced with the reduction of CH_4 content in the product stream, indicating that CH_4 decomposition (Eq. (9)) takes place. For the case of the

50%NiO/ZrO₂-Sm (Fig. 2(b)), NiO is reduced by CH_4 at temperature around 600 °C as revealed by the decrease of CH_4 together with the increase of H_2 and CO (Eq. (7)). CO_2 observed during partial oxidation reaction could be a result of reversed Boudouard reaction (Eq. (8)) similar to the 50%NiO/ZrO₂-Sg. However, after a very short period of time, CH_4 concentration in the product stream increases and then gradually reduces at temperature ca. 650 °C together with the increase of H_2 . The increase of CH_4 consumption at this temperature indicates that partial oxidation and CH_4 decomposition occur. Similar to the case of the 50%NiO/ZrO₂-Sg, at temperature greater than

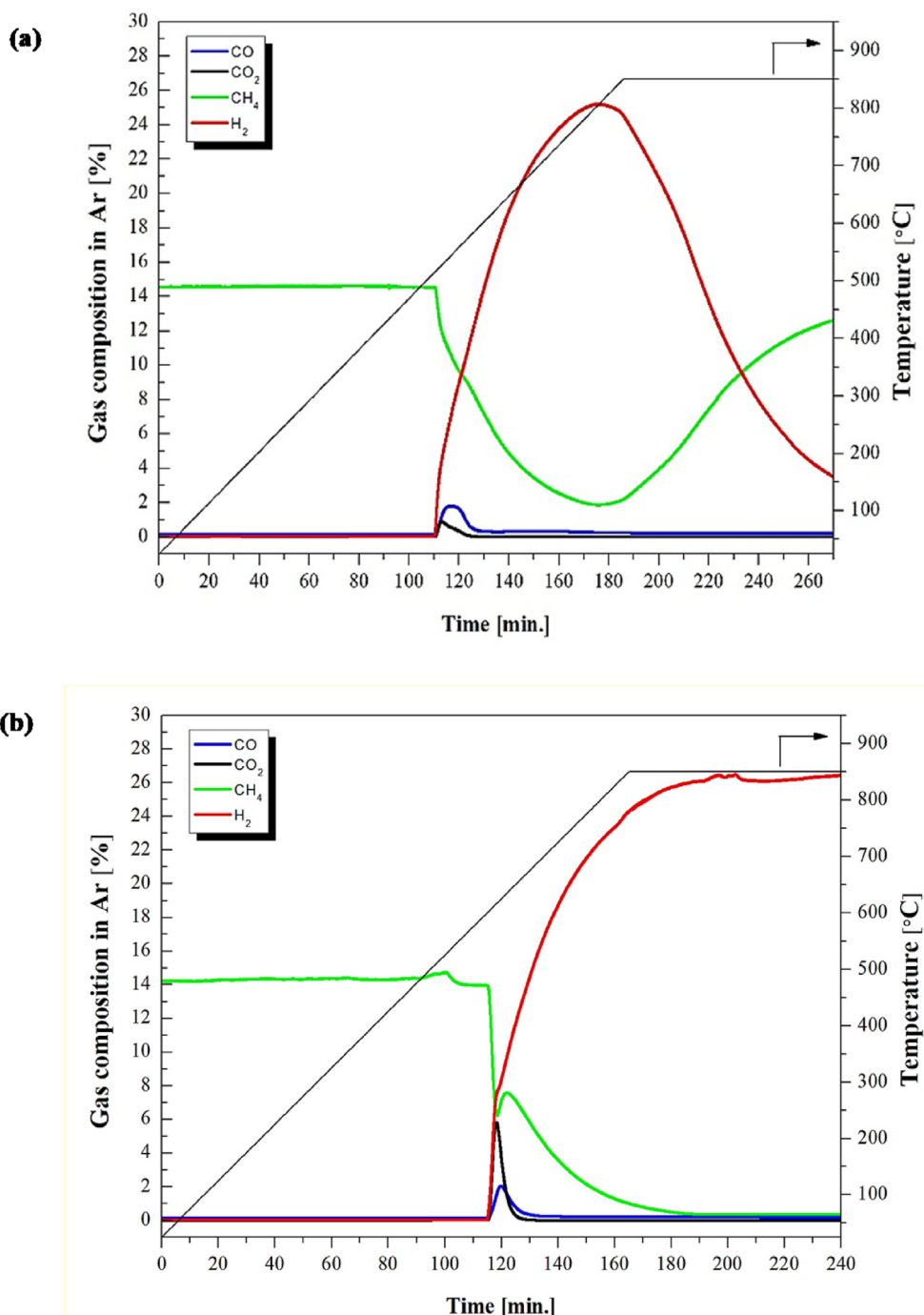
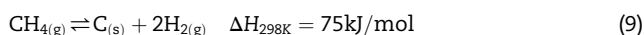
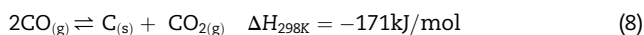
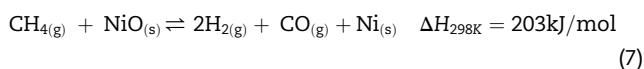


Fig. 2 – Temperature programmed surface reaction with methane (CH_4 -TPSR): (a) 50%NiO/ZrO₂-Sg and (b) 50%NiO/ZrO₂-Sm.

650 °C, only CH₄ decomposition reaction takes place. The CH₄-TPR results reveal that the 50%NiO/ZrO₂-Sg is reduced easier than the 50%NiO/ZrO₂-Sm as the temperature of the reduction is lower. This result could be attributed to greater surface area and pore volume observed with the 50%NiO/ZrO₂-Sg. In addition, greater amount of CO₂ production observed with the 50%NiO/ZrO₂-Sm demonstrates that the reversed Boudouard reaction (Eq. (8)) preferentially takes place.



As it is known that carbon usually forms on catalyst surface via DRM reaction, the performance of the developed catalyst on carbon resistance was also investigated in this work. Temperature program oxidation (O₂-TPO) was applied to examine carbon deposit on catalyst surface. The profiles in Fig. 3 reveals a peak centered at 730 °C for the 50%NiO/ZrO₂-Sm, suggesting that there is a low reactivity carbon species deposited on the catalyst. On the other hand, the O₂-TPO profile of the 50%NiO/ZrO₂-Sg shows two peaks centered at 616 and 687 °C, indicating there are two types of carbon species on the catalyst. Oxidation temperature of the 50%NiO/ZrO₂-Sm is higher than that of the 50%NiO/ZrO₂-Sg, suggesting that the 50%NiO/ZrO₂-Sm possesses lower reactivity carbon species. This result could be attributed to the presence of tetragonal ZrO₂ phase observed with the 50%NiO/ZrO₂-Sm as suggested by Zhang et al. [9] that Ni nanoparticles supported by tetragonal ZrO₂ induces low reactivity of carbon species from CH₄ decomposition to accumulate.

Amount of carbon deposited on the catalyst for the 50%NiO/ZrO₂-Sg is 0.37 g_{carbon}/g_{catalyst} and for the 50%NiO/ZrO₂-Sm is 0.36 g_{carbon}/g_{catalyst}. However, lower reactivity carbon is found with the 50%NiO/ZrO₂-Sm, resulting in the remaining of large amount of residual carbon on the catalyst.

As seen from the above results, the 50%NiO/ZrO₂-Sm could provide comparative activity for the partial oxidation and dry

reforming of biogas with the 50%NiO/ZrO₂-Sg, demonstrating the success of our developed synthesis method. The addition of urea as an N-doped carbon could prevent NiO aggregation during heat treatment step during synthesis, resulting in an enhancement of NiO–ZrO₂ interaction and a small NiO crystallite size. However, low reactivity carbon deposition is found with the 50%NiO/ZrO₂-Sm.

Effect of MgO addition

As seen in the previous section, although good activity for the partial oxidation and dry reforming of biogas could be obtained from the catalyst synthesized by our method; however, low reactivity carbon was observed. In this section, we tend to improve the performance of the 50%NiO/ZrO₂-Sm by investigating the effect of MgO addition on syngas production performance and on carbon deposition as it is known that MgO has strong Lewis basicity that can strongly induce CO₂ to adsorb and can inhibit carbon deposition [3,11,16].

XRD patterns of the 50%NiO/ZrO₂-Sg and the 50%NiO/ZrO₂/MgO-Sm catalysts, containing different amounts of MgO (ranging from 10 to 40 %wt.), are shown in Fig. 4. The results show that tetragonal ZrO₂ phase can be stabilized when MgO was added greater than 10 %wt. as the monoclinic ZrO₂ phase gradually disappears. The addition of MgO can prevent tetragonal ZrO₂ phase transformation due to the enhancement of the interaction between ZrO₂ and MgO. Our results are in agreement with that reported by Zanganeh et al. [16] who showed the similar effect of MgO addition to ZrO₂ phase. The diffraction peaks observed at 2θ = 37°, 43°, 63°, 75°, and 79° are attributed to NiO and MgO and the formation of NiO–MgO solid solution [3,20,22]. The shifted peak at 2θ ca. 63° to lower angle when the amount of MgO is increased indicates the formation of NiO–MgO solid solution [3] as demonstrated in the inset of Fig. 4

The addition of MgO results in the enhancement of BET surface area, pore size, and pore volume of the catalysts as shown in Table 3. Increasing amount of MgO enhances BET surface area and pore volume but reduces pore size of the catalyst.

Performances of the catalysts demonstrated in terms of CH₄ and CO₂ conversion, product gas composition, and H₂/CO ratio, for partial oxidation of biogas are demonstrated in Table 3 and Fig. S3. As shown in Table 3, %CO₂ conversion is not affected by the addition of MgO whereas the small effect is observed with %CH₄ conversion. High CH₄ and CO₂ conversion could be attributed to the enhancement of oxygen vacancies generated due to the interaction between MgO–ZrO₂, promoting the activation and dissociation of CO₂ for dry reforming reaction [2].

The plot of product gas composition as a function of reaction time as shown in Fig. S3 demonstrates three regions of gaseous production for the catalysts containing MgO. The production of both H₂ and CO observed with the first 15 min is due to partial oxidation of CH₄ by NiO. Then, the gaseous products drop, demonstrating the loss of oxygen carrier for the partial oxidation. After 30 min, H₂ and CO concentrations raise and reach plateau at equilibrium, which is attributed to dry reforming of CH₄. As the addition of MgO could also result in the formation of solid solution NiO–MgO, this could

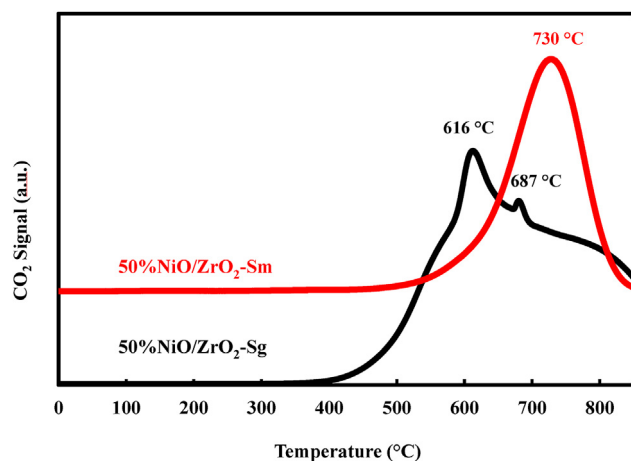


Fig. 3 – O₂-TPO profiles of the spent catalysts 50%NiO/ZrO₂-Sg and 50%NiO/ZrO₂-Sm.

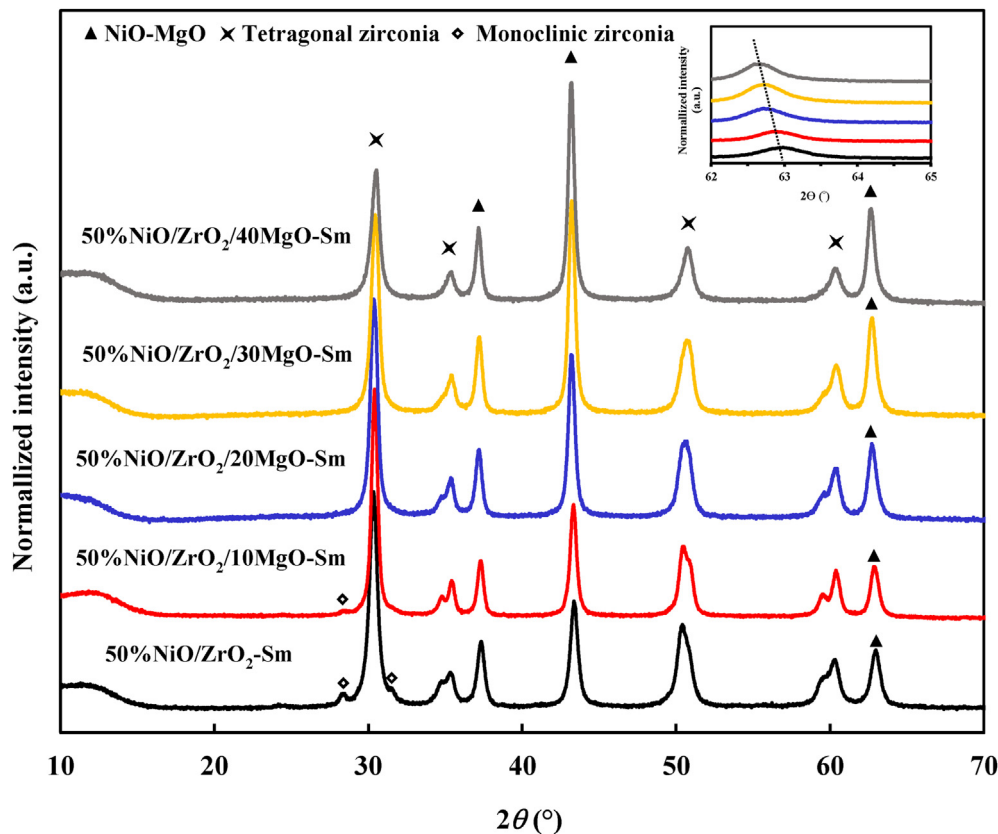


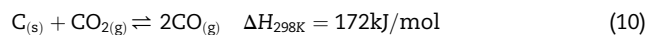
Fig. 4 – XRD patterns of fresh catalyst NiO/ZrO₂/MgO containing different amount of MgO synthesized by surface modification technique.

Table 3 – Textural properties and syngas production performances of catalysts containing different amount of MgO.

Catalysts	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)	%CH ₄ conversion	%CO ₂ conversion	H ₂ /CO	Carbon (g _{carbon} /g _{catalyst})
50%NiO/ZrO ₂ -Sm	3.59	0.04	48.39	97	100	1.9	0.36
50%NiO/ZrO ₂ /10MgO-Sm	5.63	0.07	44.59	97	100	1.9	0.33
50%NiO/ZrO ₂ /20MgO-Sm	8.19	0.08	40.25	97	100	1.7	0.31
50%NiO/ZrO ₂ /30MgO-Sm	10.1	1.07	42.21	97	100	1.7	0.33
50%NiO/ZrO ₂ /40MgO-Sm	9.90	1.02	39.90	96	100	1.7	0.31

increase the dispersion of Ni⁰ on the surface and hence facilitate the breaking of C–H bonds at active site [23,24]. Increasing MgO content results in lowering syngas quality as shown in Table 3. This could be due to the presence of MgO enhances basic property of the catalyst, which is preferential to the activation of CO₂ on catalyst surface, favoring Boudouard reaction to produce CO [3,9].

Boudouard reaction:



However, negative effect due to synergistic effect between NiO and MgO could lead to the formation of either MgO or NiO cluster as shown by the decrease of H₂ production and carbon deposition found with the 50%NiO/ZrO₂/30MgO-Sm and the 50%NiO/ZrO₂/40MgO-Sm.

Effect of NiO content

In this section, the effect of amount of NiO in the catalyst on syngas production is studied because it plays an important role as an oxygen carrier on producing H₂. Fig. 5 shows XRD pattern of catalysts containing three different amounts of NiO content (10, 30, 50 wt%). The results show that amount of NiO does not affect phase composition of the catalysts; four typical peaks at $2\theta = 30.5^\circ, 35.5^\circ, 50.9^\circ$ and 60.6° ascribed to tetragonal ZrO₂ phase and the diffraction peaks at $2\theta = 37^\circ, 43^\circ, 63^\circ, 75^\circ$, and 79° ascribed to NiO–MgO solid solution are observed with all catalysts [3,25].

Performance of the catalysts on syngas production evaluated in term of gaseous product composition (H₂ and CO) as a function of time is shown in Fig. S4. As seen, for the 10%NiO/

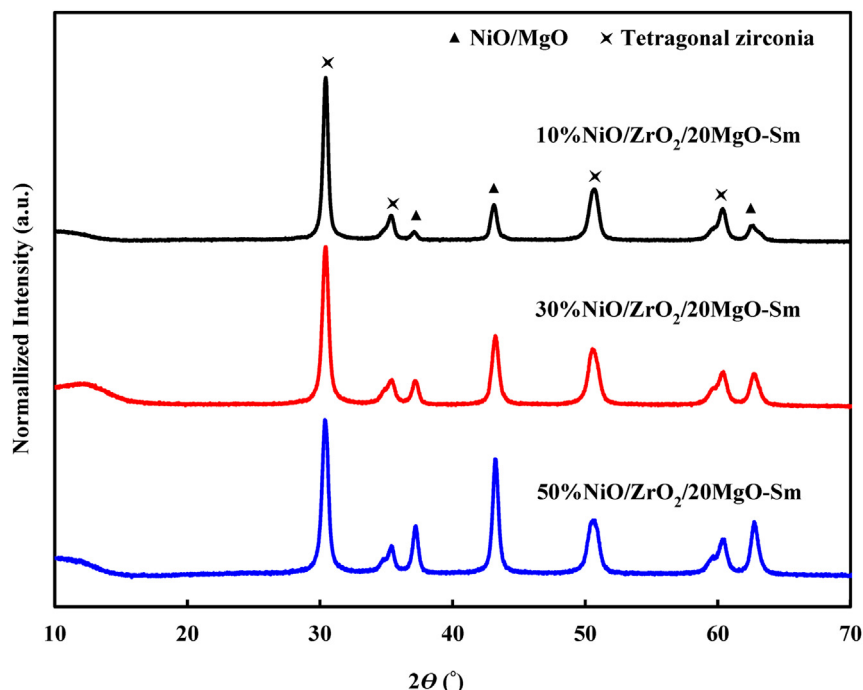


Fig. 5 – XRD patterns of the 50%NiO/ZrO₂/20MgO-Sm, 30%NiO/ZrO₂/20MgO-Sm, and 10%NiO/ZrO₂/20MgO-Sm catalysts synthesized by surface modification technique.

ZrO₂/20MgO-Sm, ca. 52% H₂ could be obtained for the first 30 min of reaction time, then gradually reduces to a plateau at ca. 39%. CO is found to be produced constantly as a function of time, which is ca. 36%. The observed result could be explained that, at the beginning of the reaction time, partial oxidation by CH₄ takes place for 30 min then the metal Ni⁰ acts as the catalyst active sites for the CH₄ dry reforming. The lowering of H₂ production after 30 min of reaction could be attributed to insufficient amount of Ni⁰ active sites to facilitate methane dry reforming reaction. With increasing amounts of NiO from 10% to 50 %wt., H₂ production increases but CO production does not significantly change. This result demonstrates the role of NiO on breaking C–H bond of CH₄. Table 4 shows %CH₄ conversion and %CO₂ conversion for the catalysts containing different NiO contents. Increasing %NiO leads to an increase of %CH₄ conversion due to high Ni⁰ active surface. Similar performance on syngas production is observed with the 30% NiO/ZrO₂/20MgO-Sm and the 50%NiO/ZrO₂/20MgO-Sm, indicating suitable range of NiO content in the catalyst. Carbon deposition is not affected by the amount of NiO in our range of

study. It is worth to note that different syngas ratio observed from our work could be employed for different downstream processes, i.e., methanol synthesis, the production of long-chain hydrocarbons or oxygenated compounds or synthetic oil via the Fischer-Tropsch process [2,26,27].

Carbon formation

As it is already known that carbon formation is a major drawback of syngas production [8,13]. In this section, we evaluate the performance of our developed catalyst 30%NiO/ZrO₂/20MgO-Sm on carbon formation occurring from the partial oxidation and dry reforming of biogas by comparing

Table 4 – CH₄ and CO₂ conversions of various NiO amounts on a ZrO₂/20MgO support.

Catalysts	CH ₄ conversion (%)	CO ₂ conversion (%)	H ₂ /CO	Carbon (mol)
10%NiO/ZrO ₂ /20MgO-Sm	54	100	1.1	0.39
30%NiO/ZrO ₂ /20MgO-Sm	96	100	2.0	0.34
50%NiO/ZrO ₂ /20MgO-Sm	97	100	1.7	0.31

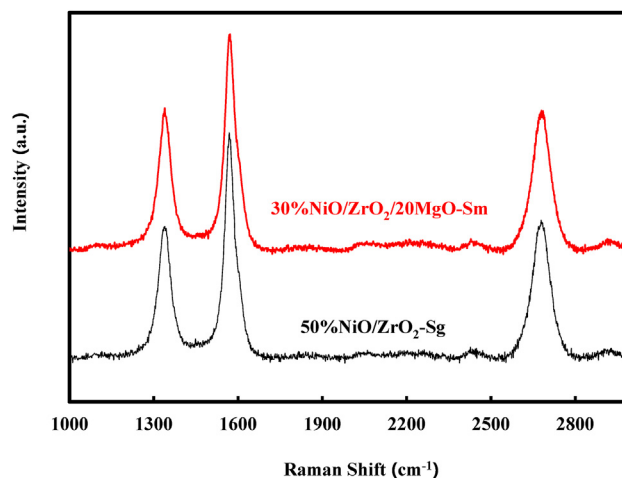


Fig. 6 – Raman spectra of spent catalysts: 30%NiO/ZrO₂/20MgO-Sm and 50%NiO/ZrO₂-Sg.

with the catalyst synthesized by sol-gel method, the 50%NiO/ZrO₂-Sg, as we used as a benchmark in section [Effect of synthesis method](#). Temperature-programmed oxidation, O₂-TPO, and Raman spectroscopy techniques were used to determine carbon deposition. The O₂-TPO profiles ([Fig. S5](#)) of the spent catalysts 30%NiO/ZrO₂/20MgO-Sm and 50%NiO/ZrO₂-Sg show a main broaden peak with a shoulder peak at temperature higher than 600 °C, corresponding to the oxidation of C_γ as suggested by Wang et al. [28]. The peak shifted to higher temperature observed with the 30%NiO/

ZrO₂/20MgO-Sm indicates higher crystallinity of carbon deposition.

Raman spectra of the spent catalysts shown in [Fig. 6](#) demonstrate 3 peaks centered at 1272 cm⁻¹ (D band), 1593 cm⁻¹ (G band), and 2680 cm⁻¹ (G' band) [12,29]. The D band is due to structural imperfections of the carbon materials, the G band is assigned to well-ordered structure of graphitic carbon due to sp² hybridization of graphite structure, and the G' band is contributed from 3D graphite regions [29]. It was proposed that the D band and the G band appears

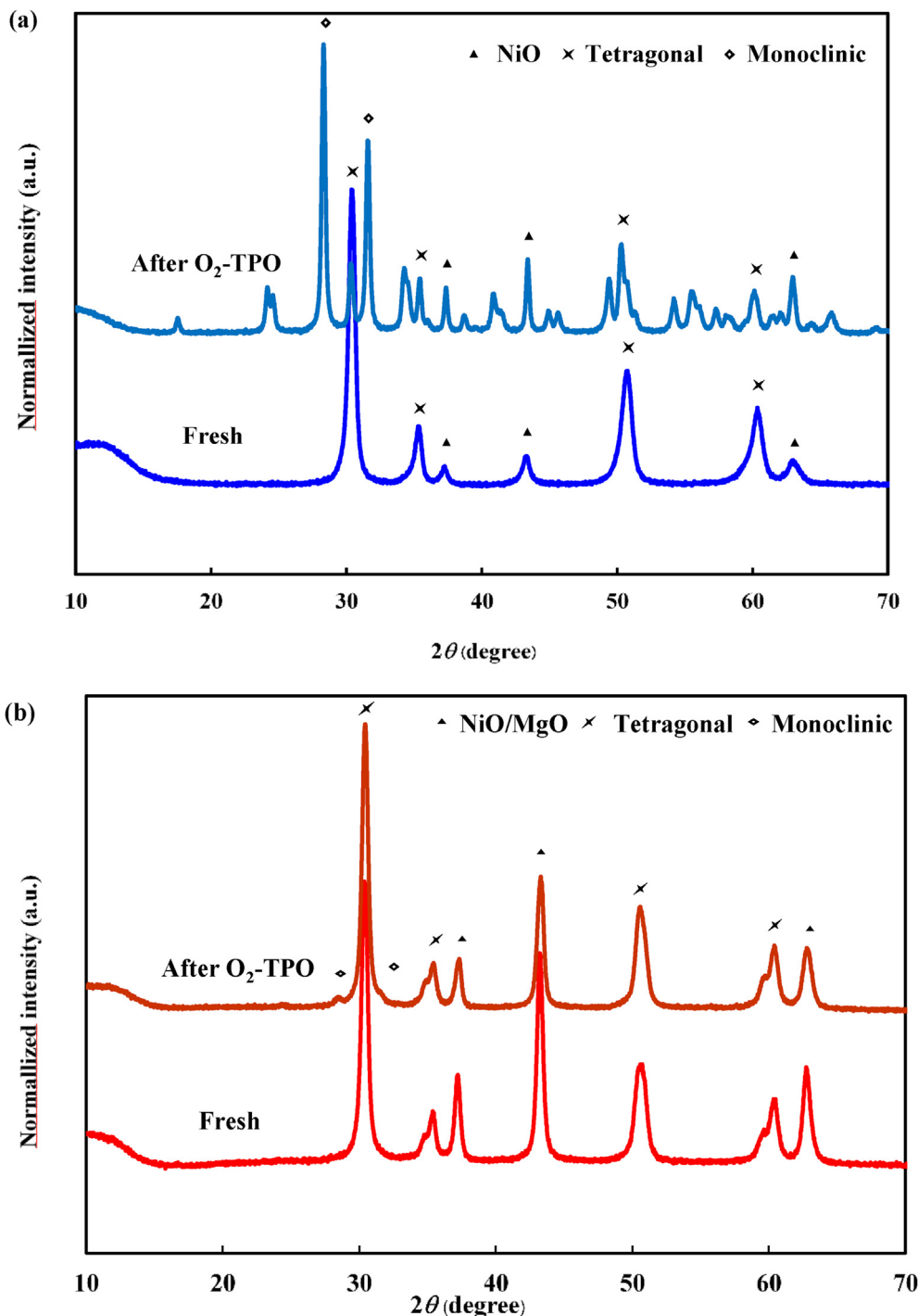


Fig. 7 – XRD patterns of (a) 50%NiO/ZrO₂-Sg and (b) 30%NiO/ZrO₂/20MgO-Sm (fresh and regenerated catalysts).

together with the G' band, revealing that the carbon structures are multi-walled carbon nanotubes (MWCNTs) [30,31]. The intensity ratios of the D/G, which represents the degree of disorder in graphite structure are 0.75 and 0.79 for the 50% NiO/ZrO₂-Sg and the 30%NiO/ZrO₂/20MgO-Sm, respectively, indicating both catalysts formed similar crystallinity graphitized carbon.

Morphology of the deposited carbon analyzed by TEM (Fig. S6) reveals the presence of MWCNTs on both catalysts, which is in good agreement with the Raman Spectra. In addition, it is also found that Ni particles are encapsulated by graphitized carbon, which is in good agreement with the TPO results that shows a shoulder peak at higher temperature [30,31].

Reactivity of our developed catalyst was investigated by examining its structure by XRD analysis after activation by oxygen through O₂-TPO compared with the fresh one. The XRD results shown in Fig. 7 reveals that crystalline structure of the 30%NiO/ZrO₂/20MgO-Sm can be maintained while the 50% NiO/ZrO₂-Sg crystalline structure collapsed. This result is attributed to the stabilization of tetragonal ZrO₂ by MgO.

Conclusion

Synthesis of NiO/MgO/ZrO₂ catalyst by simplified surface modification technique using carbon derived from urea has been shown that could apply to partial oxidation and dry reforming of biogas process for syngas production. The inclusion of MgO in the NiO/MgO/ZrO₂ catalyst played an important role in stabilizing tetragonal ZrO₂ phase and also increased basicity of catalyst surface, leading to the enhancement of catalyst activity and stability. The results of reaction tests showed that the catalysts synthesized by our developed surface modification technique could provide high CH₄ conversion, CO₂ conversion, and syngas ratio. In addition, our developed catalyst possesses high stability after regeneration, which demonstrated the success of our synthesis method. This simple synthesis technique could facilitate a large-scale production of the catalyst.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2022.03.262>.

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