



CO₂ utilization via methanation using 40%Ni/Ce_xCr_{1-x}O₂ as a novel catalyst: a comparative study of packed-bed and micro-channel reactors

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Abstract

A series of 40% Ni/Ce_xCr_{1-x}O₂ catalysts with $x=0, 0.1, 0.3, 0.5, 0.9$ and 1 were synthesized using one-pot hydrolysis method as catalysts for the methanation process. The reaction was carried out in a packed-bed and micro-channel reactors. 40 wt% Ni/Ce_{0.5}Cr_{0.5}O₂ showed the best catalytic performance towards the methanation process at 270 °C, giving 92.63% of CO₂ conversion and 90.53% of CH₄ yield. The catalyst exhibited great stability after 50 h of time-on-stream with carbon deposition around 0.0056 mg h⁻¹ was observed. The micro-channel reactor showed better performance than the packed-bed reactor in term of methane production rate which offered amount of methane production rate 109.1 mL min⁻¹ gcat⁻¹ which nearly 8 times greater than that packed-bed reactor.

Keywords CO₂ utilization · methanation process · Mixed metal oxides · Micro-channel reactor

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Introduction

One of the major causes of global warming is an increase in greenhouse gases (GHGs) emission. Carbon dioxide (CO_2) emission has been significantly increasing during the last decades [1]. Various researches focus on two main approaches to solve such problem, which are carbon dioxide capture and storage (CCS) [2, 3], and carbon dioxide utilization [4–7]. For the second approach, methanation is one of the promising reactions for converting CO_2 to methane as intermediate useful product. In this reaction, CO_2 is hydrogenated with hydrogen (H_2) giving methane (CH_4) as a product. The reaction is useful for many chemical and petrochemical processes such as; biogas ($\text{CH}_4 + \text{CO}_2$) upgrading [8], where the CO_2 in the biogas was converted to methane providing high quality methane-rich biogas, or synthesis gas purification [9], or in renewable power plant where the resulting CH_4 can be utilized further to generate electricity via combined heat and power (CHP) [10, 11]. Various previous metals have been reported as effective catalysts for the reaction such as Ru, Rh, Pd and Ni. Amongst the mentioned precious metals, Ni was so far the most interesting due to its high catalytic activity, low price, and high selectivity [12, 13]. 40% of Ni was reported to be the most suitable level of Ni as it showed the best catalytic performance and smaller crystallite size [3, 8, 12]. As for the catalyst support, CeO_2 mixed oxides such as $\text{CeO}_2\text{--Al}_2\text{O}_3$ [14], $\text{CeO}_2\text{--ZrO}_2$ [15–18], and $\text{CeO}_2\text{--Gd}_2\text{O}_3$ [19, 20], were widely utilized as a good support for methanation as ceria is well-known for its high oxygen storage capacity (OSC) in which it improves the material's redox properties. Cr_2O_3 was selected as a co-support for this work as it was reported to prevent sintering, and have an advantage in inhibiting carbon formation [21–23].

Regarding the type of the catalytic reactor, recently, the micro-channel reactor has been receiving interest for many catalytic reactions [24–31] because of their various advantages over conventional reactors. For example, their high surface to volume ratio as the result of enhancing heat and mass transfer rates which may result in increasing of productivities. With the small size of microreactor can reduce the reaction time because of the fast transport of the fluid. Also, they provide lower pressure drop if compare to conventional reactors.

In this work, 40% Ni was doped on $\text{Ce}_x\text{Cr}_{1-x}\text{O}_2$ and applied for methanation process. The effect of molar ratio between Ce and Cr on the catalytic performance was studied. A series of 40 wt% Ni/ $\text{Ce}_x\text{Cr}_{1-x}\text{O}_2$; at $x=0, 0.1, 0.3, 0.5, 0.9$, and 1; were prepared by one-pot hydrolysis method and the experiments were carried out in a lab-scaled packed-bed and micro-channel reactors for comparison.

Experimental section

Catalyst preparation

The catalysts were prepared using one-pot hydrolysis method, from which its detailed methodology was prescribed elsewhere [15]. Ce to Cr cation fraction was

defined as x and $1-x$, where x was varied at 0, 0.1, 0.3, 0.5, 0.9 and 1. Cerium(III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, ALDRICH > 99%) and Chromium(III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, ACROS > 99%) were selected as the catalyst's precursors. Ni was doped at 40% by weight to each catalyst using Nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CARLO ERBA > 99%). The obtained solid was dried overnight at 120 °C, followed by calcination in air at 500 °C for 12 h.

Stainless steel plates preparation

The micro-channel plates were made of 316L stainless steel. Each plate has 14 semi-rectangular channels of 0.37 mm width, 0.3 mm depth, and 51 mm length. Prior to the coating process, the stainless steel plates were first cleaned with 20% citric acid in an ultrasonic bath for 30 min and afterwards calcined at 800 °C for 2 h to generate a thin oxide layers for catalyst adhesion on the stainless steel plates.

Catalyst coating

The suspension was prepared by dissolved polyvinyl alcohol (PVA) in deionized water while stirred at 65 °C for 3 h. The solution was set and left overnight. The catalysts powder and acetic acid were added to the solution with the weight ratio of PVA to water to catalyst powder to acetic acid was 5 to 84 to 10 to 1. The suspension was stirred at 65 °C for 3 h, then cooled to room temperature and continuously stirred for 3 days until a homogenous suspension was obtained.

The gas distribution area, inlet and outlet area of the micro-channel plates were sealed by polymer film before coating. The micro-channel plates were then filled with the prepared suspension by wash-coat and the excess suspension was wiped-off. The coated plates were dried at room temperature for 4 h and in an oven at 120 °C overnight, then calcined at 500 °C for 3 h at 1 °C min⁻¹ of heating rate. Two coated plates were sealed together by welding. 1/8 inches stainless steel tubes were attached to the coated plates as an inlet and outlet by welding.

Catalyst characterization

The catalyst crystallinity was characterized using X-ray diffraction (XRD) technique (Bruker AXS D8 diffractometer). Diffraction patterns were recorded using Cu K_α ($\lambda = 1.5418 \text{ \AA}$) at 40 kV of voltage and 30 mA of anode current with scanning step size of 0.02° every 0.5 s in a range of $20^\circ < 2\theta < 70^\circ$. H_2 temperature programmed reduction (H_2 -TPR) was applied to determine the optimal reduction temperature. 500 mg of catalyst was loaded into a quartz tube reactor (i.d. = 10 mm, o.d. 13 mm.). The reactor was heated from room temperature to 900 °C at 5 °C min⁻¹ of heating rate in the presence of 2% H_2/Ar at a total gas flow of 100 mL min⁻¹. The gaseous products were real-time analyzed by an online mass spectrometer (Omnistar GSD 320 O serie). The morphology of stainless steel plates were characterized using scanning electron microscopy (SEM) (SU-8230, Hitachi, Japan). The amount of carbon deposit was determined using a thermogravimetric analyzer (TG) (Mettler

Toledo). 7 mg of the catalyst sample was performed in 100 mL min^{-1} of oxygen. The temperature was increased flow of from room temperature to 1000°C at $10^\circ\text{C min}^{-1}$ of heating rate.

Experimental procedure and calculation

The catalysts were sieved to $75\text{--}180 \mu\text{m}$ for quartz tubular packed-bed reactor and less than $38 \mu\text{m}$ for micro-channel reactor. The weight of catalyst was 200 mg and 65.4 mg for the packed-bed and the micro-channel reactor. The catalyst was placed inside the quartz tubular packed-bed reactor (i.d.=4 mm) where quartz wool was placed at the top and the bottom of bed for immobilization. The packed-bed and the micro-channel reactor were placed in the middle of an electrical furnace with 30 cm of heating zone. Prior to the reaction, the catalyst was reduced in 40% H_2/Ar at 500°C for 90 min and then cooled down to 230°C . A mixture of H_2 and CO_2 (molar ratio $\text{H}_2/\text{CO}_2=4:1$) was afterwards introduced into the reactor with the operating temperature was varied from 230 to 400°C while the pressure was kept at atmospheric. The gaseous product stream was analyzed using gas chromatography (Shimadzu, GC-2014ATF). CO_2 conversion, CH_4 yield, and CH_4 selectivity were calculated using the following equations:

$$\text{CO}_2\text{conversion}(\%) = \frac{[\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}}{[\text{CO}_2]_{\text{in}}} \times 100 \quad (1)$$

$$\text{CH}_4\text{yield}(\%) = \frac{[\text{CH}_4]}{[\text{CO}_2]_{\text{in}}} \times 100 \quad (2)$$

$$\text{CH}_4\text{selectivity}(\%) = \frac{[\text{CH}_4]}{[\text{CH}_4] + [\text{CO}]} \times 100 \quad (3)$$

$$\text{CH}_4\text{productionrate}(\text{ml. min}^{-1} \text{ g}_{\text{cat}}^{-1}) = \frac{[\text{CH}_4]}{\text{catalystweight}} \quad (4)$$

Here $[\text{CO}_2]_{\text{in}}$ and $[\text{CO}_2]_{\text{out}}$ represent volumetric flow rate of CO_2 in (mL min^{-1}) at the inlet and the outlet, respectively. $[\text{CH}_4]$ stands for volumetric flow rate of the produced CH_4 at the outlet.

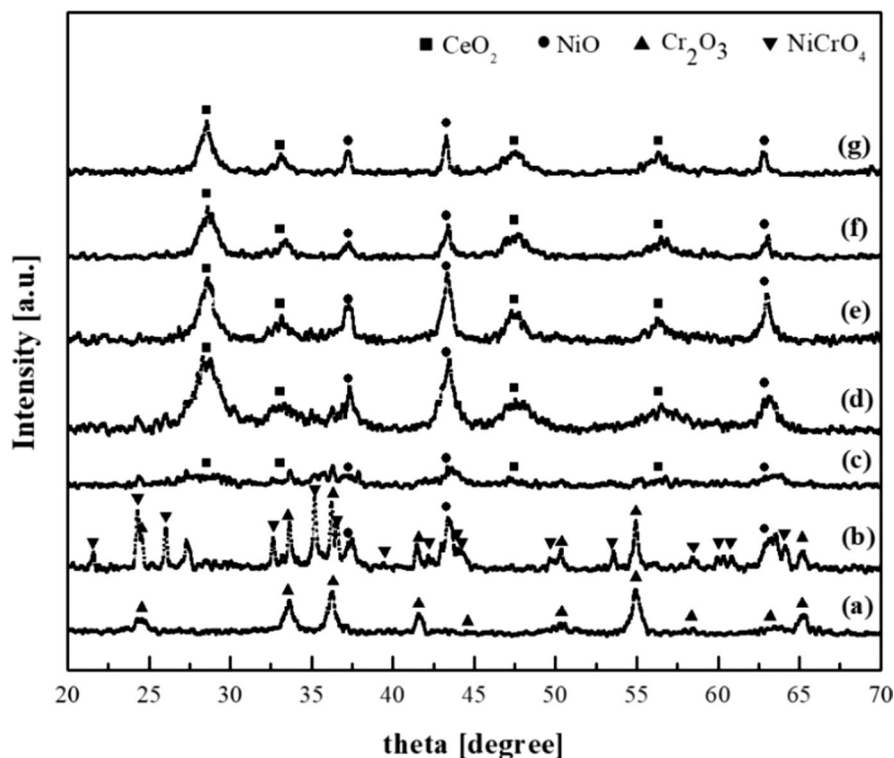


Fig. 1 XRD patterns of the catalysts calcined at 500 °C; pure Cr_2O_3 (a) and the 40% $\text{Ni}/\text{Ce}_x\text{Cr}_{1-x}\text{O}_2$ with $x = 0$ (b), $x = 0.1$ (c), $x = 0.3$ (d), $x = 0.5$ (e), $x = 0.9$ (f), and $x = 1$ (g)

Results and discussion

Catalyst characterization

XRD

The X-ray diffraction (XRD) patterns of pure Cr_2O_3 and the 40 wt% $\text{Ni}/\text{Ce}_x\text{Cr}_{1-x}\text{O}_2$, where $x = 0, 0.1, 0.3, 0.5, 0.9$, and 1 , are shown in Fig. 1. Pure Cr_2O_3 showed the diffraction peaks at $2\theta = 24.57^\circ, 33.54^\circ, 36.34^\circ, 41.58^\circ, 44.60^\circ, 50.38^\circ, 54.94^\circ, 58.36^\circ, 63.20^\circ$, and 65.19° , corresponded with other research [32]. All the prepared catalysts showed NiO crystalline phase where 2θ was shown at $37.27^\circ, 43.29^\circ$, and 62.91° , corresponding to (1 1 1), (2 0 0), and (2 2 0) planes. At $x = 0$, mixed oxides Cr_2O_3 and NiCrO_4 were observed. However, they became less visible when the Ce content increased from $x = 0.1$ to 1 , suggesting that $\text{Ce}_x\text{Cr}_{1-x}\text{O}_2$ was formed as a minor crystalline phase. This phase was fully overlapped within CeO_2 major crystalline phase, when Ce level was higher [18], where the diffraction peaks were shown at $2\theta = 28.55^\circ, 33.08^\circ, 47.50^\circ$, and 56.33° . Average NiO crystallite size was estimated

from the main NiO (200) reflection peak, using Scherrer equation. The NiO crystallite size of the 40 wt%Ni/Ce_xCr_{1-x}O₂ catalysts when x=0, 0.1, 0.3, 0.5, 0.9, and 1 was calculated at 11.45, 8.68, 8.20, 10.58, 17.05, and 20.19 nm. It can be concluded that the NiO crystallite size tended to increase with increasing Ce content.

H₂-TPR

The reducibility of pure NiO and other 40% Ni/Ce_xCr_{1-x}O₂ catalysts were studied using H₂-TPR technique, as demonstrated in Fig. 2. Pure NiO showed two main reduction peaks, centered at 386.7 °C and 499.1 °C, attributing to the reduction of Ni³⁺ to Ni²⁺ and Ni²⁺ to metallic nickel (Ni⁰) [33–35]. At x=0, the reduction peak of NiO was shifted to higher temperature at 391.4 and 677.6 °C due to interaction between Ni and Cr in NiCrO₄, assigned to reduction of Cr⁶⁺ to Cr³⁺ [36, 37]. However, three main reduction peaks were observed when X=0.1 to 0.9. At X=0.3 to 0.9, the first two peaks of the Ni reduction were shifted to lower temperatures, suggesting that these certain levels of CeO₂ could lower the reduction temperature of the catalyst's system [38, 39]. The third peak was found at temperature higher than 900 °C, associated to the reduction of mixed Ce_xCr_{1-x}O₂ [38]. At X=1, two reduction peaks were found at 324.6 °C and 505.7 °C, assigned to the reduction of NiO and Ni which interacted with CeO₂ [16, 38, 40]. It can be concluded that (1) Ce addition encouraged lower reduction temperature of NiO, from 386.7 to 362.7 (x=0.3), 323.3 (x=0.5), 326.3 (x=0.9) and 324.6 °C (x=1.0) (2) Cr addition

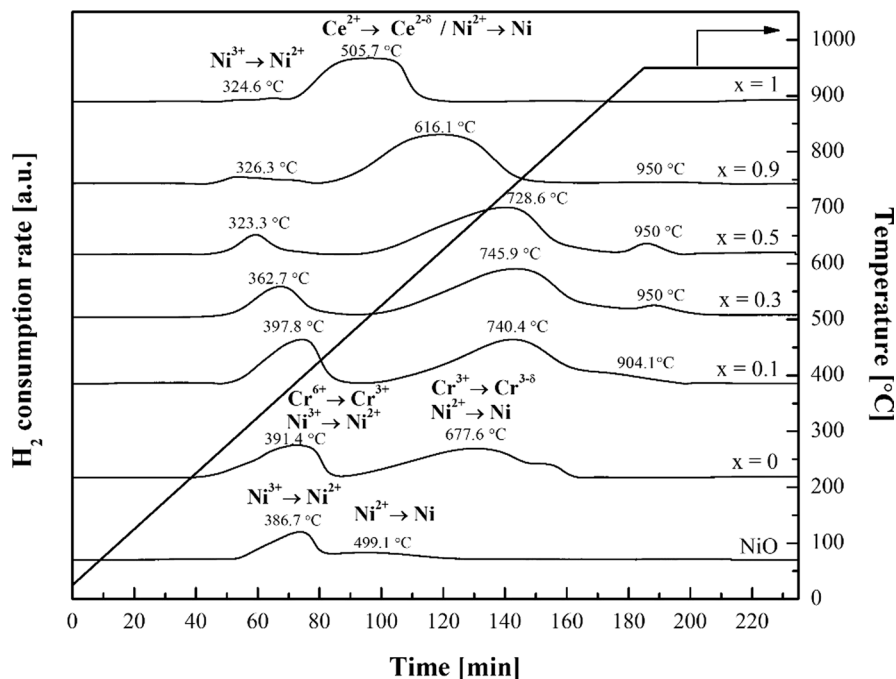


Fig. 2 H₂-TPR profiles of pure NiO and 40 wt%Ni/Ce_xCr_{1-x}O₂ catalysts with different X value

caused the opposite effect as it increased the reduction temperature of NiO from 386.7 to 391.4 °C. In this work, all the catalysts therefore were reduced at 500 °C, to completely reduce and activate NiO [15, 21].

SEM

Fig. 1Sa and Fig. 1Sb show the surface morphology of the prepared micro-channel plates after cleaning with citric acid and after annealing at 800 °C. It can be seen that the oxides on the surface were generated by annealing process which believed for good catalyst adhesion on stainless steel plates in catalyst coating process.

Catalytic performance of CO₂ methanation in packed-bed reactor

Effect of Ce/Cr ratio

The catalytic performance of all prepared catalysts was studied at temperature ranging from 230 to 350 °C. CO₂ conversions and CH₄ yields are presented in Figs. 3 and 4. CO₂ conversions were found to increase when the temperature increased,

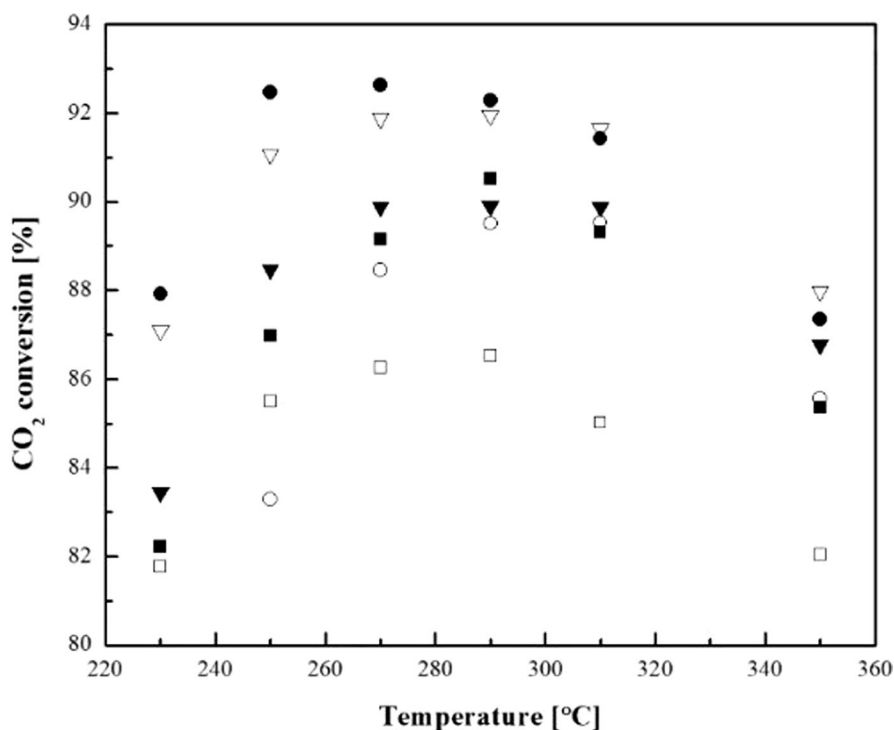


Fig. 3 CO₂ conversion for CO₂ methanation at different temperature for the 40 wt%Ni/Ce_xCr_{1-x}O₂ with x = 0 (○), x = 0.1 (■), x = 0.3 (▽), x = 0.5 (●), x = 0.9 (□), and x = 1 (▼) over temperature range of 230–350 °C, at H₂/CO₂ = 4:1

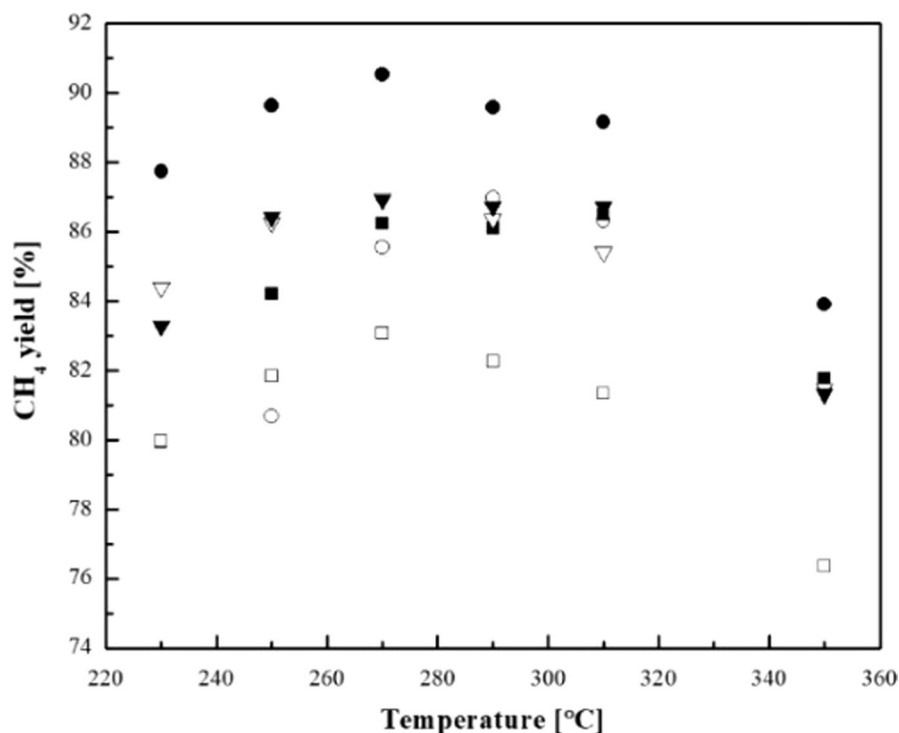


Fig. 4 CH_4 yield for CO_2 methanation at different temperature for the 40 wt%Ni/Ce $_x$ Cr $_{1-x}$ O $_2$ with $x = 0$ (○), $x = 0.1$ (■), $x = 0.3$ (▽), $x = 0.5$ (●), $x = 0.9$ (□), and $x = 1$ (▼) over temperature range of 230–350 °C, at $\text{H}_2/\text{CO}_2 = 4:1$

until reached the maximum values at approximately 270 °C. At higher temperature, CO_2 conversions started to decrease due to the reaction's thermodynamic limitation. The results were in good agreement with previous works reported by other researchers [20, 41]. It was found that the 40% Ni/Ce $_{0.5}$ Cr $_{0.5}$ O $_2$ displays the highest catalytic performance amongst all the catalysts when operated at 270 °C, offering 92.63% of CO_2 conversion, 90.53% of CH_4 yield. Both CO_2 conversion and CH_4 yield were maximized when the ratio of Ce to Cr was equal ($x = 0.5$). This is well-agreed with H_2 -TPR's results where the reduction peak of NiO occurred at the lowest temperature (323.3 °C) when $x = 0.5$. The lower reduction temperature suggested that the catalyst has higher reducibility [18, 44, 45]. However, further addition of Ce from 0.5 to 1.0 resulted in a drop in CO_2 conversion and CH_4 yield. This is due to the coverage effect of excess CeO $_2$ on Ni ^{0} active site [42, 43].

Effect of weight hourly space velocity (WHSV)

40%Ni/Ce $_{0.5}$ Cr $_{0.5}$ O $_2$ was selected for further study. The weight hourly space velocity (WHSV) was varied at 27,000, 54,000, and 82,560 mL g $^{-1}$ h $^{-1}$ by applying the total flow rate at 90, 180, and 275 mL min $^{-1}$. Fig. 5 shows CO_2 conversion and CH_4 yield,

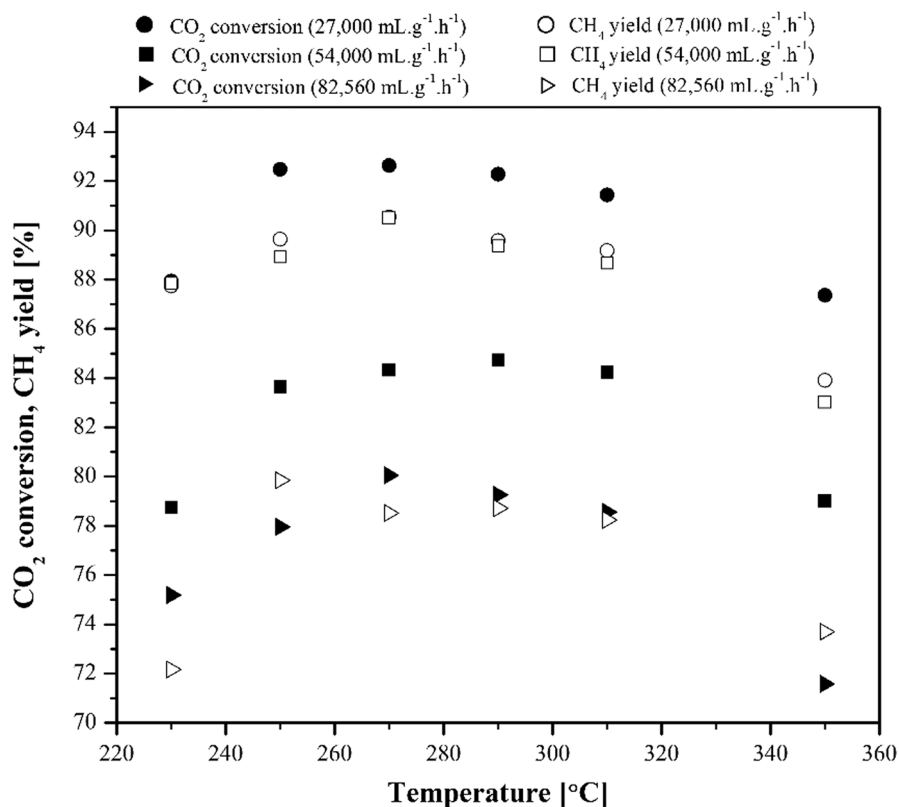


Fig. 5 CO₂ conversion and CH₄ yield obtained from CO₂ methanation in the presence of 40%Ni/Ce_{0.5}Cr_{0.5}O₂ at WHSV of 27,000, 54,000, and 82,560 mL g⁻¹ h⁻¹ over temperature range of 230–350 °C, at H₂/CO₂ = 4:1

versus reaction temperature. An increase in WHSV resulted in a decrease in both CO₂ conversion and CH₄ yield, implying that the reaction equilibrium concentration was not reached as the residence time became shorter by the higher WHSV. At WHSV of 54,000 mL g⁻¹ h⁻¹, CH₄ yield was calculated to be 4% higher than CO₂ conversion, approximately, possibly due to CO₂ adsorption and/or some errors from numerical methods. CO₂ conversion and CH₄ yield were found to reach maximum value at 80.05% and 79.85% at WHSV of 82,560 mL g⁻¹ h⁻¹. CH₄ selectivity was found to be more stable at lower WHSV (27,000 mL.g⁻¹.h⁻¹). It should be noted that the catalyst in this study showed better performance compared to other previous studies [46, 47] where they reported that ~80% of CO₂ conversions and ~70% of CH₄ yields were achieved at higher temperature at 300 or 330 °C.

Table 1 compares the catalyst performance between this work and other recent catalysts reported by other researchers. 40%Ni/Ce_{0.5}Cr_{0.5}O₂ catalyst was found to be a superior catalyst due to its outstanding catalytic performance at lower operating temperature, even at the higher WHSV.

Table 1 Catalysts comparison for CO₂ methanation reaction

Catalyst	Reactor type	WHSV (mL·g ⁻¹ ·h ⁻¹)	Temp. (°C)	CO ₂ conv. (%)	CH ₄ sel. (%)	Ref
1.71%Mn-15%Ni/ Al ₂ O ₃	Packed-bed	48,000	400	80	95	[48]
20%Ni/H-Al ₂ O ₃	Packed-bed	9,600	290	95	99	[49]
10%La-20%Ni/ Al ₂ O ₃	Packed-bed	9,000	350	80	100	[50]
15%Ni-2%CeO ₂ / Al ₂ O ₃	Packed-bed	15,000	350	85	99	[43]
10%Ni/CeO ₂ -ZrO ₂	Packed-bed	20,000	300	55	97	[17]
30%Ni-5%Fe- Al ₂ O ₃	Packed-bed	9,600	220	58.5	58	[51]
2wt%Ce-20Ni/ Al ₂ O ₃	Packed-bed	9,000	350	80.30	100	[52]
30wt%Ni-5wt%Fe/ Al ₂ O ₃	Packed-bed	9,000	350	70.63	98.87	[53]
Ni-20wt%CeO ₂ / MCM-41	Packed-bed	9,000	380	85.6	99.8	[42]
20Ni/Al ₂ O ₃	Packed-bed	9,000	350	82.4	100	[54]
40%Ni/ Ce _{0.5} Cr _{0.5} O ₂	Packed-bed	27,000	270	92.63	100	This work
40%Ni/ Ce _{0.5} Cr _{0.5} O ₂	Packed-bed	82,560	270	80.05	100	This work

Stability test

The stability of 40%Ni/Ce_{0.5}Cr_{0.5}O₂ catalyst was experimented at 270 °C. As shown in Fig. 6, approximately 93% of CO₂ conversion and CH₄ yield were achieved for the entire reaction time of 50 h. The post-exposure catalyst was examined using XRD characterization, as shown in Fig. 2S. The absent of NiO crystalline phase (where 2θ was shown at 37.27°, 43.29°, and 62.91°) proved that the catalyst was completely reduced prior the reaction. The XRD pattern of used catalyst revealed that Ni⁰ was stable and remained in its metallic form after the reaction, evidenced by the diffraction peak at 2θ = 44.8° and 52.2° (JCPDS 4-850) [55]. CeO₂ peaks were also remained unchanged, indicating that the catalyst system was stable. The amount of carbon deposition on the used catalyst was determined by means of TG as shown in Fig. 3S. The weight of fresh and used catalysts increased at temperature higher than 320 °C. This suggested that the Ni was reoxidized back to its original state of NiO [56, 57]. Approximately 4% difference of both TG curves was observed, indicated that the carbon deposit which equal to 0.0056 mg h⁻¹. The carbon deposition was occurred via CO₂ adsorption and CO₂ dissociation on the catalyst's surface [58]. TGA measurement was carried out as a post-exposure experiment to investigate trace of CO and CO₂.

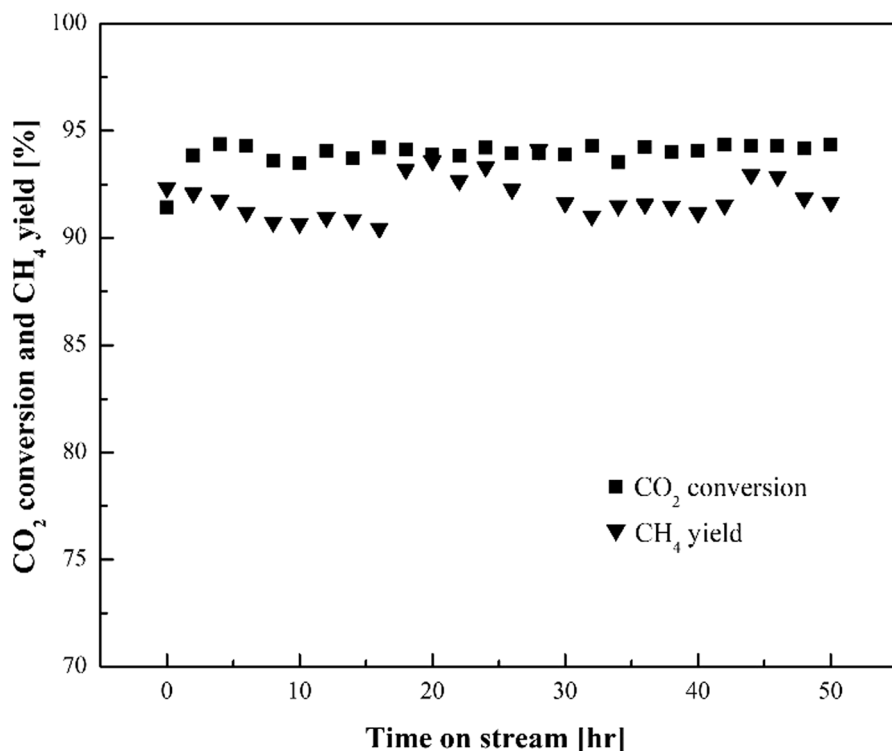


Fig. 6 Stability test over 40%Ni/Ce_{0.5}Cr_{0.5}O₂ catalyst towards CO₂ methanation, the reaction was run for 50 h at 270 °C, H₂/CO₂ = 4:1, WHSV = 27,000 mL g⁻¹ h⁻¹

Catalytic performance of CO₂ methanation in Micro-channel reactor

Effect of weight hourly space velocity (WHSV)

The influence of weight hourly space velocity (WHSV) on CO₂ methanation was investigated using 40%Ni/Ce_{0.5}Cr_{0.5}O₂ catalyst operated in micro-channel reactor. WHSV was varied at 55,045, 82,560, and 119,266 mL g⁻¹ h⁻¹ by applying the total flow rate at 60, 90, and 130 mL min⁻¹, while varying the operating temperature between 250–400 °C. From Fig. 7, it can be seen that the activity increased with an increase in WHSV up to 82,560 mL g⁻¹ h⁻¹ and decreased to 119,266 mL g⁻¹ h⁻¹. This is because of the shorter contact time as a result of decreasing of adsorbed reactant on the catalyst. This result is in good agreement with previous work reported by other researchers [59, 60]. They reported that increasing in WHSV resulting in a drop in catalytic performance. The optimal condition for micro-channel reactor was therefore at WHSV of 82,560 mL g⁻¹ h⁻¹ at 350 °C offering 83.93% of CO₂ conversion, 81.08% of CH₄ yield, 95.85% of CH₄ selectivity.

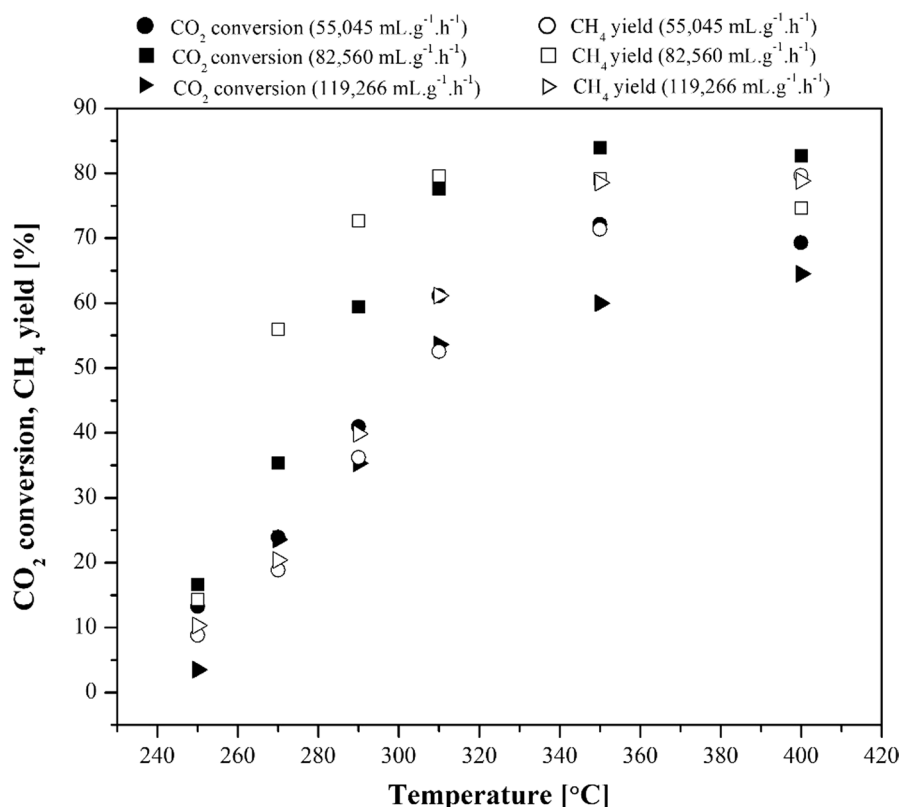


Fig. 7 CO₂ conversion and CH₄ yield obtained from CO₂ methanation in the presence of 40%Ni/Ce_{0.5}Cr_{0.5}O₂ at WHSV of 55,045, 82,560 and 119,266 mL g⁻¹ h⁻¹ over temperature range of 250–400 °C, at H₂/CO₂ = 4:1 operated in micro-channel reactor

Effect of stainless-steel on catalytic performance

Uncoated catalyst in micro-channel reactor was also tested to study the effect of stainless-steel micro-channel reactor. WHSV at 82,560 mL.g⁻¹.h⁻¹ was selected for this study. Fig. 8 shows the catalytic performance with CO₂ conversion, CH₄ yield, and CO yield. CO₂ conversion was proved that the stainless-steel has an effect on the catalytic reaction. At temperature of 400 °C found stainless-steel provides about 20% CO₂ conversion, it could explain by the effect of formation of oxides after annealing could be involved. It was clearly seen that the catalyst coated micro-channel provides higher CH₄ yield with lower CO yield while the uncoated catalyst micro-channel shows less amount of CH₄ yield with higher CO yield. It was suggested that coated catalyst micro-channel is preferable for CO₂ methanation ($\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$) while uncoated catalyst micro-channel is promote of reverse water gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$).

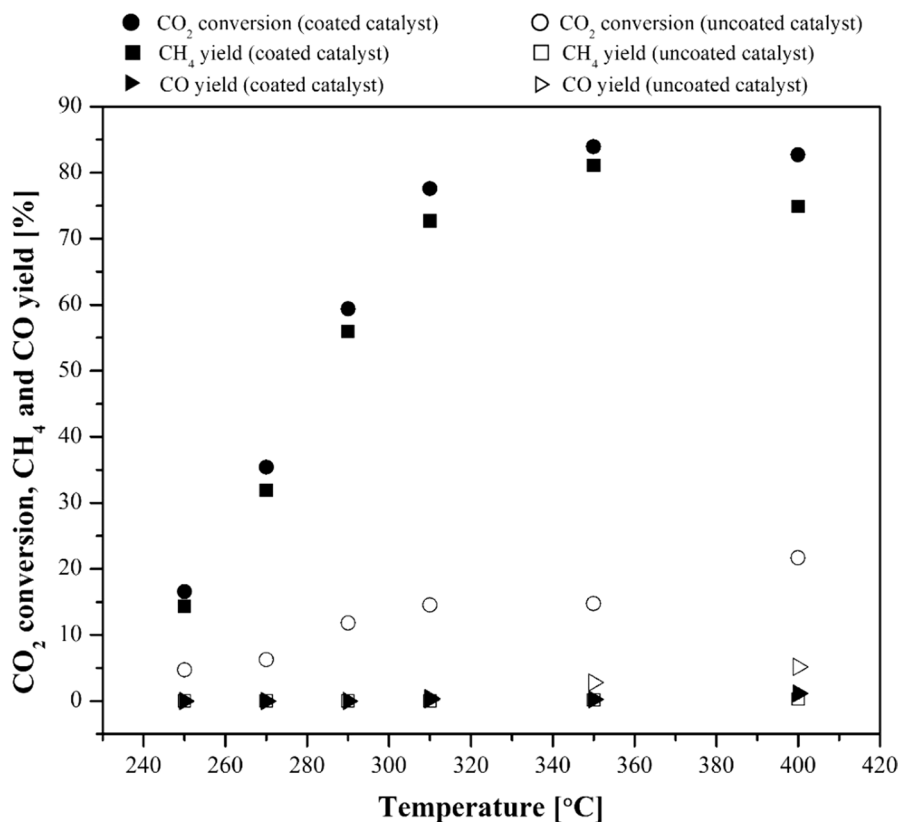


Fig. 8 CO₂ conversion, CH₄ yield, and CO yield; obtained from CO₂ methanation with uncoated catalyst and coated catalyst in micro-channel reactor over temperature range of 250–400 °C, at H₂/CO₂ = 4:1

Catalytic performance comparison for packed-bed and micro-channel reactor

CO₂ methanation via both packed-bed and micro-channel reactors were compared at the same WHSV with the highest catalytic performance for each reactor as shown in Table 2. It was clearly seen that the major product which is methane was obtained from micro-channel reactor which nearly 8 times greater than that packed-bed reactor. This was suggested that the benefit of its high surface to volume ratio of micro-channel reactor, leading to enhancing higher mass transfer rate as a result of higher amount of methane productivity.

Table 2 The highest catalytic performance for each packed-bed and micro-channel reactor at WHSV of 82,560 mL g⁻¹ h⁻¹

Reactor	CO ₂ conv. [%]	CH ₄ yield [%]	CH ₄ production rate [mL min ⁻¹ gcat ⁻¹]
Packed-bed	80.05	78.52	14.03
Micro-channel	83.93	81.08	109.1

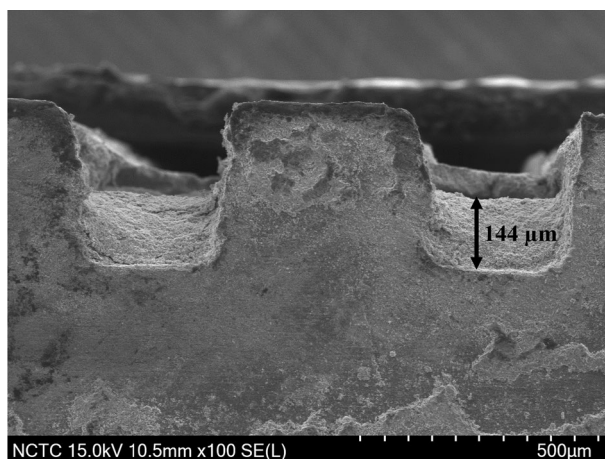


Fig. 9 Surface morphology of the micro-channel plates analyzed using SEM technique after catalyst coating process

Moreover, for further development of micro-channel reactor to increase more catalytic performance, the catalyst coating step should be focused. Due to in this work has a limitation problem in catalyst coating step. It can be coated the catalyst with the height of 144 microns as shown in Fig. 9 which cannot full fill with the maximum height of 300 microns. If it can be coated cover it, it could be achieved higher mass transfer rate and could enhance more catalytic performance.

Conclusions

40%Ni/Ce_{0.5}Cr_{0.5}O₂ catalyst was found to be a superior catalyst for CO₂ methanation, due to its high CO₂ conversion and CH₄ yield (92.63% and 90.53%) when operated in packed-bed reactor. The catalyst was found to be active at 270 °C, which was lower than the operating temperatures of other recently developed catalysts. The catalyst was stable after 50 h test. 40%Ni/Ce_{0.5}Cr_{0.5}O₂ is therefore proposed here as a novel catalyst for CO₂ utilization through the methanation process. The micro-channel reactor showed nearly 8 times higher methane production rate compared with packed-bed reactor when operated at the same WHSV. This was the result of the high surface to volume ratio which can be enhanced more mass transfer rate of reactant.

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