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CO₂ Hydrogenation to Synthetic Natural Gas over Ni, Fe and Co-Based CeO₂–Cr₂O₃

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Abstract: CO₂ methanation was studied over monometallic catalyst, i.e., Ni, Fe and Co; on CeO₂-Cr₂O₃ support. The catalysts were prepared using one-pot hydrolysis of mixed metal nitrates and ammonium carbonate. Physicochemical properties of the pre- and post-exposure catalysts were characterized by X-ray Powder Diffraction (XRD), Hydrogen Temperature Programmed Reduction (H₂-TPR), and Field Emission Scanning Electron Microscope (FE-SEM). The screening of three dopants over CeO₂-Cr₂O₃ for CO₂ methanation was conducted in a milli-packed bed reactor. Ni-based catalyst was proven to be the most effective catalyst among all. Thus, a group of NiO/CeO₂-Cr₂O₃ catalysts with Ni loading was investigated further. 40 % NiO/CeO₂-Cr₂O₃ exhibited the highest CO₂ conversion of 97.67% and CH₄ selectivity of 100% at 290 °C. The catalytic stability of NiO/CeO₂-Cr₂O₃ was tested towards the CO₂ methanation reaction over 50 h of time-on-stream experiment, showing a good stability in term of catalytic activity.

Keywords: synthetic natural gas; CO₂ methanation; Ni-based catalysts; CeO₂-Cr₂O₃ catalyst

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1. Introduction

Global warming has caused several serious impacts on the environment in recent years. Increasing CO₂ emission is anthropogenic in origin and is the main cause of global warming. Nowadays, many studies focused on two strategies to reduce atmospheric CO₂ concentration; through carbon capture and CO₂ conversion to biofuels [1,2]. The captured CO₂ can be utilized and converted into fuels and chemicals via chemical processes such as dry reforming of methane for synthesis gas production, or CO₂ hydrogenation to CH₄, methanol or higher alcohols [3]. CO₂ methanation is one of the promising processes which involves carbon recycle from abundant CO₂. Methane, as a product of CO₂ hydrogenation, is considered versatile and flexible as it can be injected directly into existing natural gas pipelines, or utilized as a raw material for chemical production [4]. This CO₂ hydrogenation can be looked at as Power-to-Gas process (PtG) by its means to store (and transport) energy in the form of natural gas [5]. The process refers to a conversion of renewable electricity to a gaseous energy carrier via two pathways: (1) H₂ production by water electrolysis, where wind or solar energy technologies could be integrated; and (2) H₂ conversion to CH₄, by methanation reaction with external CO₂ capture [6]. CO₂ methanation was firstly discovered and proposed as the Sabatier reaction: CO₂ + 4H₂ ⇌ CH₄ + 2H₂O, ΔH_r²⁹⁸ = -164.8 kJ·mol⁻¹ [7]. Although the reaction is highly exothermic and thermodynamically

avored at high pressures/low temperatures (<400 °C) [4,8], there are significant kinetic limitations due to the high stability of CO₂. Furthermore, heat accumulation from the reaction generally causes severe hotspots in the reactor, due to the heat transfer limitation within the process, leading to the catalyst deactivation and shortened catalyst lifespan [9]. Moreover, low operating temperature is favorable for CO disproportionation reaction ($2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$, $\Delta H_{r,298} = -172.4 \text{ kJ}\cdot\text{mol}^{-1}$), resulting in unwanted coke deposition. In order to obtain the highest possible methane yield, it is necessary to invent a catalyst which enhances the reaction's activity, withstands sintering and counters the coking phenomenon. Various active metals (such as Ni, Fe, Co, Ru, Rh, and Pd) have been used as an active site while metal oxides (such as CeO₂, La₂O₃, MgO, γ -Al₂O₃, SiO₂, TiO₂, and ZrO₂) have been useful as a support in a catalyst system for the CO₂ methanation reaction [3,10–13]. Amongst these materials, CeO₂ is so far found to be the most interesting support due to its high oxygen storage capacity (OSC) and its ability to disperse the active site [14]. In addition, CeO₂ could promote the interaction between support and metal active component, such that the growth and dispersion of the metal active particles can be well distributed and controlled throughout the surface of the support, leading to the higher CO₂ conversion [15]. The number oxygen vacancy can be tailor-made by substituting smaller transition metal ions (e.g., chromium ions) into CeO₂. The higher number of lattice oxygen can combust coke deposits and reduce the chance of sintering [13,16–18]. According to previous research, Ni-, Fe-, Co doped on CeO₂ have shown relatively high activities for CO₂ methanation and possessed high stability when tested for 15 to 50 h reaction times [19–23].

In this work, Ni-, Fe- and Co- based CeO₂/Cr₂O₃ were prepared using the one-pot hydrolysis method. The level of metal loading, operating temperature, reduction temperature and other relevant variables were observed as all of these parameters are well-known to influence the catalytic performance of the catalysts [24,25]. The physicochemical properties of the synthesized catalysts were examined, comparing pre- and post-exposure by X-Ray Diffractometer (XRD), Hydrogen Temperature-Programmed Reduction (H₂-TPR), and Field Emission Scanning Electron Microscopes (FE-SEM). The catalyzation of CO₂ methanation was conducted in a milli-packed bed reactor under atmospheric pressure where the operating temperature was varied from 200 to 350 °C. The reduction temperatures of 500 and 700 °C were chosen (via H₂-TPR) for comparison purposes. WSHV was fixed at 27,624 mL·h⁻¹·g_{cat}⁻¹, and the stoichiometric reactants ratio was kept at 4 for all the experiments.

2. Methodology

2.1. Catalyst Powder-Formed Preparation

Forty percent (by weight) x/CeO₂-Cr₂O₃ (where x = Ni, Fe, and Co) catalysts were synthesized by a single step preparation using (NH₄)₂CO₃ (PANREAC, 30% NH₃) as a hydrolysis agent, the details of which are outlined in [3]. The relevant nitrate precursors Ni(NO₃)₂·6H₂O (CARLO ERBA, Cornaredo, Italy, ≥99.0%), Fe(NO₃)₃·9H₂O (UNIVAR, Donners Grove, IL, UAS, ≥99.0%), Co(NO₃)₂·6H₂O (CARLO ERBA, ≥99.0%), Ce(NO₃)₃·6H₂O (ALDRICH, St. Louis, MO, USA, ≥99.0%), and Cr(NO₃)₂·6H₂O (ACROS, Merelbeke, Belgium, ≥99.0%) were dissolved in 50 mL distilled water where the ratio of active metal (Ni, Fe, and Co) to support (1 to 1 of CeO₂/Cr₂O₃) was fixed at 40 to 60 by weight. Two molar (NH₄)₂CO₃ solution was gradually dropped into the nitrate solutions until the pH reached 8.8–9.0. The mixture was continuously stirred while heated to 80 °C for 3 h. The solution's temperature was then raised again to 120 °C to evaporate water and a dark blue gel was slowly obtained. The resulting material was then calcined in moving air at 500 °C with 10 °C/min of heating for 24 h before the black powder of the catalyst was achieved. The catalyst powder was then pressed, crushed, and sieved to gain its uniform particle size ranging from 75 to 180 μm in order to avoid pressure drop that could occur across the catalyst bed.

2.2. Characterizations

XRD analysis (Malvern PANalytical diffractometer) was performed using CuK α radiation (with $\lambda = 1.5418 \text{ \AA}$, 40 kV, 15 mA). The diffractogram patterns were recorded over 2-theta ranging from 10 to 80° with a scanning speed of 0.02° per second. The catalyst's phase structures were identified using JCPDS cards (Joint Committee on Powder Diffraction Standards).

The optimal reduction temperature of the catalyst was screened using an in situ H₂-TPR technique which was carried out in our lab-scale conventional packed-bed reactor, connected to a Quadrupole Mass Spectrometer (PFEIFFER, MS, Omnistar GSD 320, HAKUTO) operated in a SEM-MID mode. A total of 0.5 g of the catalyst sample was packed in a quartz tube reactor (i.d. = 10 mm) and pre-treated in 10% O₂/Ar at 500 °C for 1 h, followed by Ar purging to clean the catalyst's surface from any possible absorbed impurities. After the system reached ambient temperature, 5 % H₂/Ar was introduced through the catalyst's bed with a total flowrate of 100 mL·min⁻¹ while the temperature was elevated to 950 °C at 5 °C/min.

Surface morphology and micro-structure of the catalysts, both pre- and post-exposure, were investigated using a Field Emission Scanning Electron Microscopes (FE-SEM, SU-8230 Hitachi, Japan) with an accelerating voltage of 15 kV.

2.3. CO₂ Methanation Activity in a Packed-Bed Reactor

CO₂ methanation was performed in a tubular packed-bed reactor under atmospheric pressure. A total of 0.2 g of catalyst was placed between two layers of quartz wool in the middle of the reactor (i.d. = 4 mm). The catalyst was reduced in 100 mL·min⁻¹ of pure H₂ for 2 h at the achieved reduction temperature (from H₂-TPR where NiO reduced to metallic Ni at 500 °C while Co₂O₃ and Fe₃O₄ reduced to metallic Co and Fe at 850 °C) from the prior reaction. Next, the process was cooled down to the desired operating temperature, varying at 200, 210, 230, 250, 270, 290, 310, and 350 °C. Ar was purged in between to remove any excess H₂. The mixture of gaseous reactant, CO₂:H₂:Ar at a ratio of 1:4:5 by volume, was injected through the catalyst's bed. Total flow rate was set at 90 mL·min⁻¹, giving WSHV at 27,624 mL·h⁻¹·g_{cat}⁻¹. Moisture was condensed as a by-product using a cooler oil bath at the bottom of the reactor. After the process approached equilibrium, the dried gas products were automatically analyzed using gas chromatography coupled with a TCD detector (Shimadzu GC-2014ATF) every 7 min for 1 h. CO₂ conversion (X_{CO_2}), CH₄ selectivity (S_{CH_4}), and CH₄ yield (Y_{CH_4}) were calculated using the following formulas:

$$CO_2 \text{ conversion, } X_{CO_2} [\%] = \left(\frac{F_{CO_2}^{in} - F_{CO_2}^{out}}{F_{CO_2}^{in}} \right) \times 100\% \quad (1)$$

$$CH_4 \text{ selectivity, } S_{CH_4} [\%] = \left(\frac{F_{CH_4}}{F_{CH_4} + F_{CO}} \right) \times 100\% \quad (2)$$

$$CH_4 \text{ yield, } Y_{CH_4} [\%] = \frac{X_{CO_2} \times S_{CH_4}}{100} \quad (3)$$

$F_{CO_2}^{in}$ and $F_{CO_2}^{out}$ represent volumetric flow rate of CO₂ in the feed stream and outlet stream, respectively, whereas F_{CH_4} and F_{CO} denote the volumetric flow rate of the product gas stream, CH₄ and CO, respectively.

3. Results and Discussion

3.1. Characterizations

3.1.1. XRD

XRD patterns of all the fresh catalysts (calcined in moving air at 500 °C) were achieved as shown in Figure 1. CeO₂-Cr₂O₃ (■), as major crystals, were found in all samples and appeared to possess fluorite cubic structure [26], having two-theta position peaks at 28.57, 33.12, 47.49, 56.38, 58.94, 69.42, 76.74, 79.33, 88.44, and 95.34°. All the dopants, NiO (●), Fe₂O₃ (◆), and Co₃O₄ (▲) appeared as minor crystalline phases as shown in Figure 1a–c, respectively. NiO peaks were found at 37.31, 43.35, 63.00, and 75.49° (JCPDS No. 01-073-1519); whereas Fe₂O₃ peaks appeared at 24.19, 33.28, 35.68, 40.99, 49.57, 54.32, 62.64, and 64.15 (JCPDS No. 01-076-4579); and Co₃O₄ peaks were detected at 33.06, 36.67, 44.59, 59.08, and 64.92 (JCPDS No. 01-078-5631). Pure phase Cr₂O₃ was found in Co₃O₄-CeO₂-Cr₂O₃ at 36.34, 44.60, 58.357, and 63.204° (JCPDS No. 00-001-1294), indicating that Cr₂O₃ cannot fully incorporate into the CeO₂ lattice. This inhomogeneous solid solution depends on the size of ionic radii of the solutes. The ionic radius of Ce³⁺ appeared the largest (1.101 Å), followed by Cr³⁺ (0.80 Å) and Co⁴⁺ (0.61 Å) [27,28]. Thus, the Co⁴⁺ ion was able to compete with Cr³⁺ in becoming embedded into the CeO₂ lattice, creating CeCoO₃ perovskite [27,29], as it can be seen in Figure 1c. This phenomenon could cause a decay in the catalyst's catalytic performance due to the loss of active sites, in this case, Co₃O₄. In addition, the average crystallite size of the NiO, Fe₂O₃, and Co₃O₄ on CeO₂-Cr₂O₃ were calculated using the Scherrer's equation at 14.56, 25.03, and 25.60 nm, respectively. The smaller active site could perhaps accommodate reactants better, rendering the chance of higher catalytic performance.

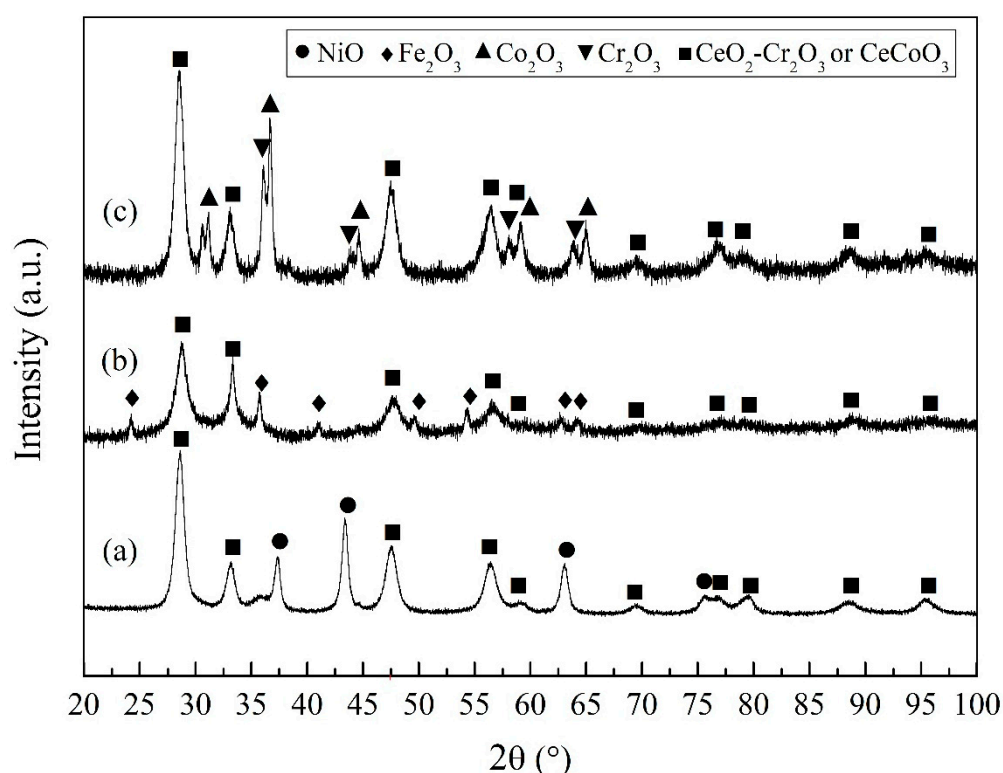


Figure 1. XRD patterns of (a) 40% NiO/CeO₂-Cr₂O₃, (b) 40% Fe₂O₃/CeO₂-Cr₂O₃, and (c) 40% Co₃O₄/CeO₂-Cr₂O₃ after calcined at 500 °C, where NiO (●), Fe₂O₃ (◆), Co₃O₄ (▲), Cr₂O₃ (▼), and CeO₂-Cr₂O₃ (■) phases.

3.1.2. H₂-TPR

Figure 2 shows the reduction profiles of pure CeO₂ (a), CeO₂-Cr₂O₃ (b), NiO/CeO₂-Cr₂O₃ (c), Fe₂O₃/CeO₂-Cr₂O₃ (d), and Co₃O₄/CeO₂-Cr₂O₃ (e) catalysts. Pure CeO₂ (a) had 2 small reduction peaks at 570 and >950 °C, corresponding to the surface reduction and bulk reduction of CeO₂, respectively [30]. The first reduction peak of CeO₂-Cr₂O₃ (b) appeared at 480 °C, where Cr⁶⁺ ions were reduced to Cr³⁺ ions. The reduction peak at 565 °C and >950 °C corresponded to the reduction of CeO₂-Cr₂O₃ at surface and bulk oxygen, respectively [30–33]. Substitution of Cr₂O₃ into CeO₂ was reported to enhance oxygen vacancy of the catalyst system [16,18,34], in which its H₂ consumption was proven to be significantly higher than the pure CeO₂.

Three distinct peaks at 325, 675, and 940 °C were found for NiO/CeO₂-Cr₂O₃ catalyst (c). The first two peaks were identical to the reduction of Ni³⁺ to Ni²⁺ and to the reduction of Ni²⁺ to metallic nickel, respectively [34–36]. Some reduction of Cr⁶⁺ ions to Cr³⁺ ions could be combined in the first peak, whereas the second and the third peaks represented the reduction of the Cr₂O₃ incorporated within the CeO₂ structure at the surface and bulk level, respectively. For Fe₂O₃/CeO₂-Cr₂O₃ (d), the first peak appeared at 395 °C, representing the reduction of Cr⁶⁺ ions to Cr³⁺ ions, whereas its second and third peaks at 505 and 940 °C were attributed to the reduction of CeO₂-Cr₂O₃ at the surface and bulk levels, respectively. The two reduction peaks observed at 505 °C and between 700 to 950 °C also represented the reduction of Fe₂O₃ to Fe₃O₄ and reduction of Fe₃O₄→FeO→metallic Fe, respectively [37,38]. Co₂O₃/CeO₂-Cr₂O₃ (e) was detected at 445, 700, and >950 °C, and associated with 1) the reduction of Cr⁶⁺ ions to Cr³⁺ ions, 2) the reduction of Co³⁺ ions to Co²⁺ ions and the reduction of CeO₂-Cr₂O₃ (and/or CeCoO₃ perovskite) with surface oxygen, and 3) the reduction of Co²⁺ ions to metallic Co, and the reduction of CeO₂-Cr₂O₃ (and/or CeCoO₃ perovskite) with bulk oxygen [39]. The catalyst's oxygen deficiency and number of active sites were interpreted from the hydrogen consumption, which was compared amongst all the catalysts and ordered as: NiO/CeO₂-Cr₂O₃ > Fe₂O₃/CeO₂-Cr₂O₃ > Co₂O₃/CeO₂-Cr₂O₃.

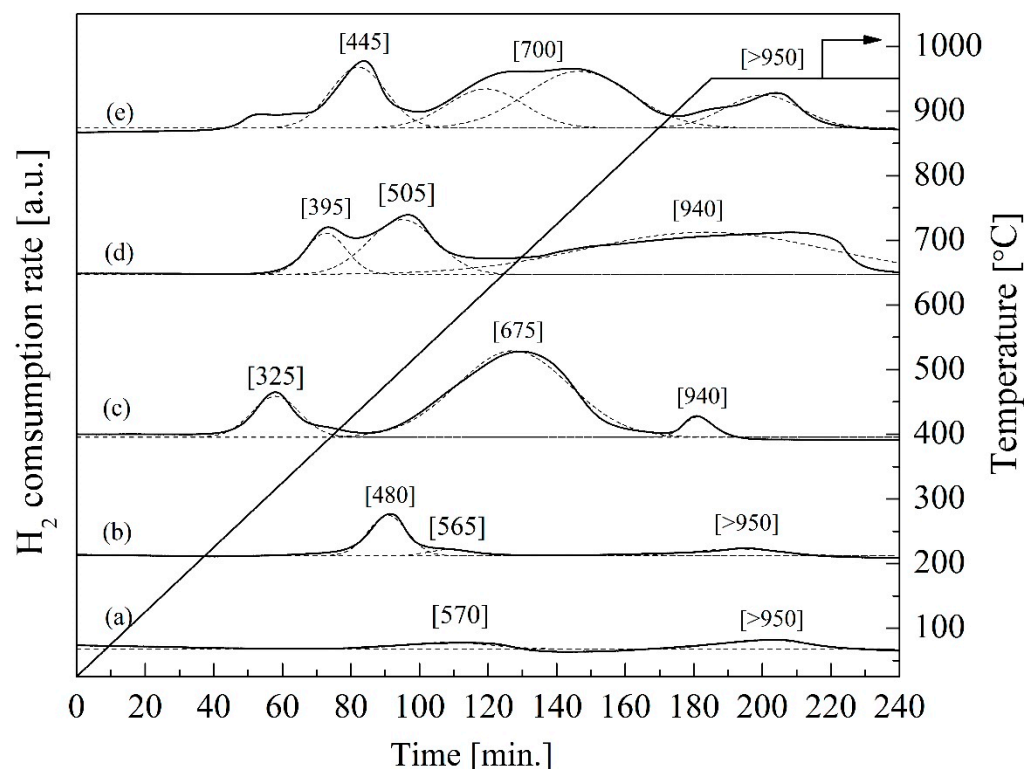


Figure 2. H₂-TPR profiles of (a) pure CeO₂, (b) CeO₂-Cr₂O₃, (c) 40%wt. NiO/CeO₂-Cr₂O₃, (d) 40%wt. Fe₂O₃/CeO₂-Cr₂O₃, and (e) 40%wt. Co₂O₃/CeO₂-Cr₂O₃ catalyst calcined at 500 °C.

3.2. Catalytic Performance Test

3.2.1. Choice of the Monometallic

Catalytic performance, in terms of CO₂ conversion (Figure 3 (left)) and CH₄ selectivity (Figure 3 (right)), of all the prepared catalysts was determined at various operating temperatures, ranging from 200 to 350 °C. CO₂ conversion tended to increase with increasing temperature for all catalysts. Amongst all the selected metals, Ni was proven as the best monometallic active site for CeO₂-Cr₂O₃, considering CO₂ conversion, which was much higher than other metals (Fe and Co) starting at 260 °C. The highest CO₂ conversion over Ni/CeO₂-Cr₂O₃ was achieved at 290 °C, giving CO₂ conversion of 90.19%. However, CO₂ conversion decreased when the temperature was higher than 330 °C, due to its thermodynamic limitation [3,40,41]. In terms of CH₄ selectivity, Ni also showed the best performance by giving complete selectivity at 100% during all temperatures (from 200 to 360 °C), followed by Fe which offered 94% of CH₄ selectivity at its equilibrium at 290 °C. On the other hand, catalytic performance of Co as the monometallic dopant was incomparable to that of the other two, as it gave no reaction at low temperature (below 260 °C) and reached its maximum at 24% of CH₄ selectivity at 270 °C. The CH₄ selectivity was decreased at temperatures higher than 270 °C. This was due to the formation of CO as an unwanted product from the reverse water-gas shift reaction [19,42].

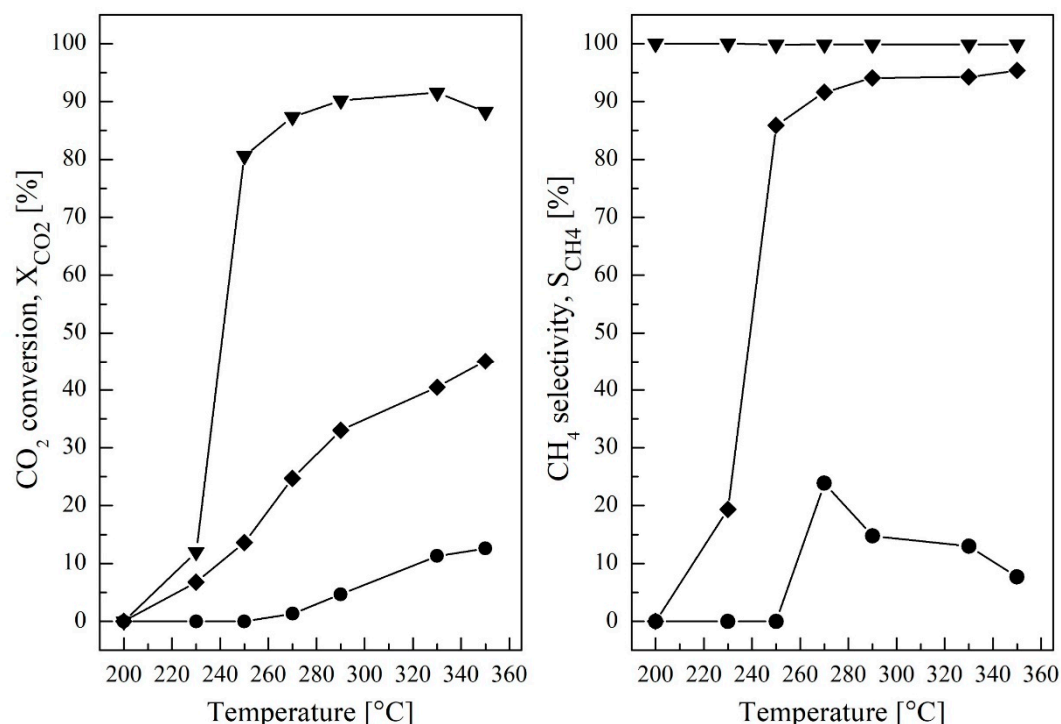


Figure 3. Catalytic performance of CO₂ methanation in terms of CO₂ conversion (Left) and CH₄ selectivity (Right) over different metals: (▼) Ni; (◆) Fe; and (●) Co; on CeO₂-Cr₂O₃ support.

3.2.2. Effect of Metal Content on Catalytic Performance

The influence of metal content, doped on CeO₂-Cr₂O₃, towards CO₂ methanation was investigated over Ni-/CeO₂-Cr₂O₃, where the Ni level was varied at 10, 20, 30, 40 and 50% by weight. Figure 4 showed that the percentage of all the selected Ni contents exhibited the same trend, where CO₂ conversion was increased with increasing temperature and increasing amount of Ni content. The nickel content represented the amount of the active

site for CO₂ methanation reaction, thus, the higher level of Ni was unsurprisingly improved the efficiency of the reaction [41,43–45]. However, excess Ni loading could cause other problems, i.e., pore blockage, coagulation and obstruction of nano-channels [46–48]. For this reason, there was only a small difference in CO₂ conversion, between using 40% and 50% Ni loading.

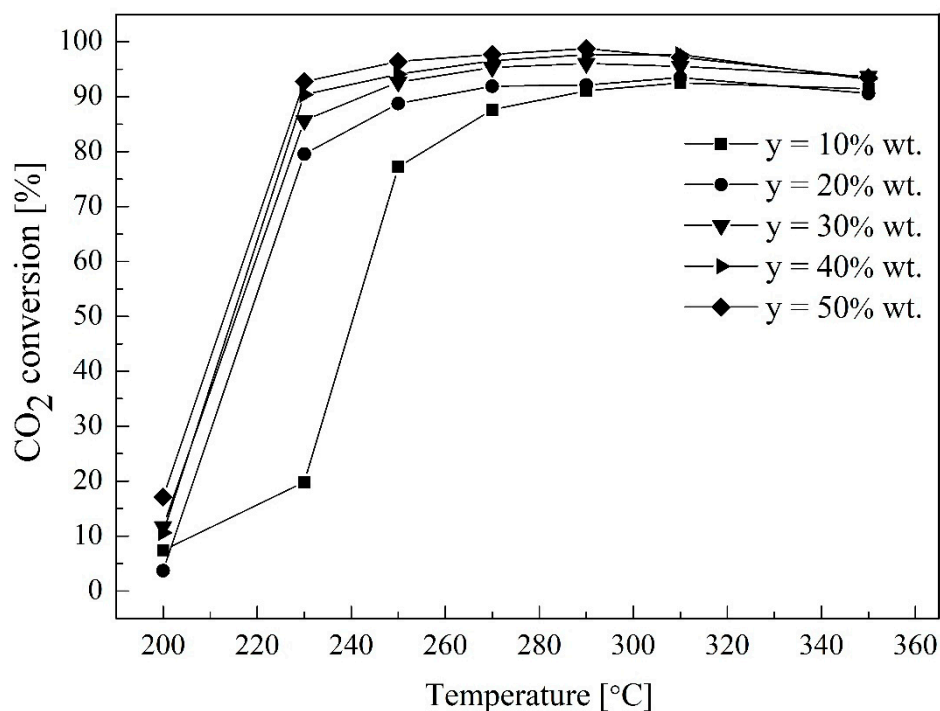


Figure 4. Catalytic performance of y %wt. NiO/CeO₂-Cr₂O₃ catalyst for CO₂ methanation.

3.2.3. Effect of Reduction Temperature on Catalytic Performance

Two different reduction temperatures, at 500 and 700 °C, were selected for this study. Figure 5 presents relationship between CO₂ conversion and reduction temperature of the catalyst at different operating temperatures. The results showed that the catalyst which reduced at 500 °C gave the highest CO₂ conversion for all of the temperature ranges, compared to the one reduced at 700 °C. In addition, the decrease in CO₂ conversion at the higher reduction temperature (700 °C) could also be the effect of the catalyst's sintering, resulting in a lower number of active sites [49].

3.3. Catalytic Stability

The catalytic stability of the NiO/CeO₂-Cr₂O₃ was measured in term of CO₂ conversion and CH₄ selectivity, illustrated in Figure 6. Approximately 97% of CO₂ conversion and 100% of CH₄ selectivity were achieved and maintained during 50 h of reaction time. XRD and SEM techniques were utilized for pre- and post-exposure characterization. XRD patterns of fresh NiO/CeO₂-Cr₂O₃ catalyst was compared with the post-exposure one after the stability test, shown in Figure 7. Although both look quite similar, a decrease in full-width half-maximum (FWHM) was clearly noticed, indicating catalyst sintering. Compared to pre-exposure, post-exposure crystallite size was found to have increased from 11 to 13 nm, whereas particle size was doubled from 313 to 612 nm. However, the sign of sintering or deactivation was not clearly observed in TOS experiment. This could be due to the fact that the rate of reaction is rapid, to the point that the catalyst surface area becomes relatively less significant. No NiO peak was found on the diffraction pattern in either the pre- or post-exposure, indicating that the catalyst was fully reduced as peaks

appeared at 44.508, 51.847, and 76.372 (JCPDS No. 00-004-0850). However, surface morphology of the pre- and post-exposure catalyst were found to be different, as shown in Figure 8. It can be seen that the particle size of the catalyst became larger after reaction due to its agglomeration, in an attempt to reduce its surface free energy.

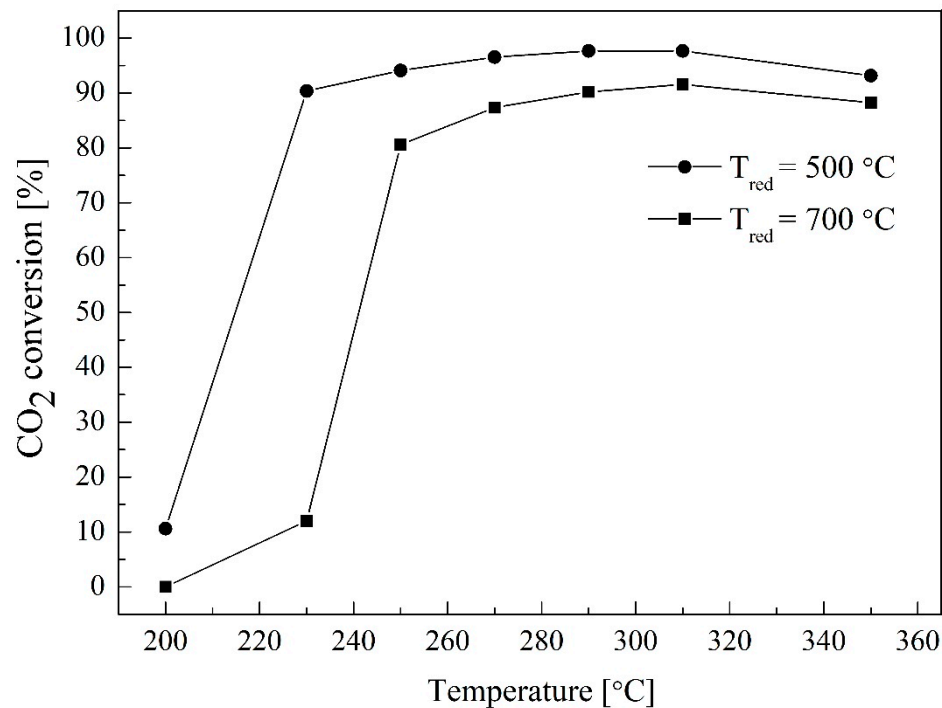


Figure 5. The catalytic performance with different reduction temperature using Ni-based on CeO₂-Cr₂O₃ catalyst.

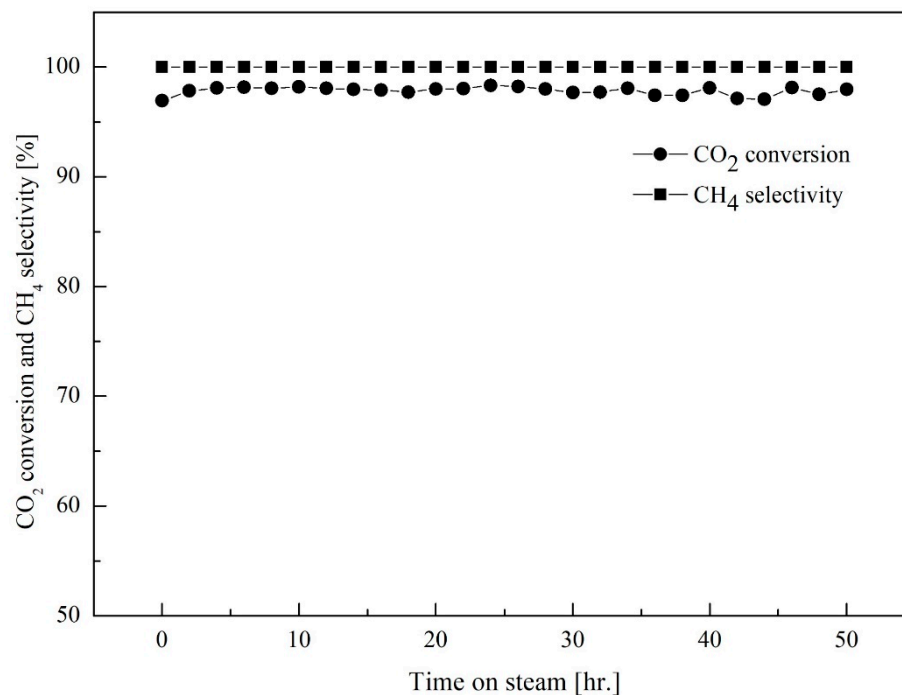


Figure 6. Time on steam of 40%wt. NiO/CeO₂-Cr₂O₃ after H₂/CO₂ = 4:1 exposure at 290 °C and 27,624 mL.h⁻¹.g_{cat}⁻¹ for 50 h.

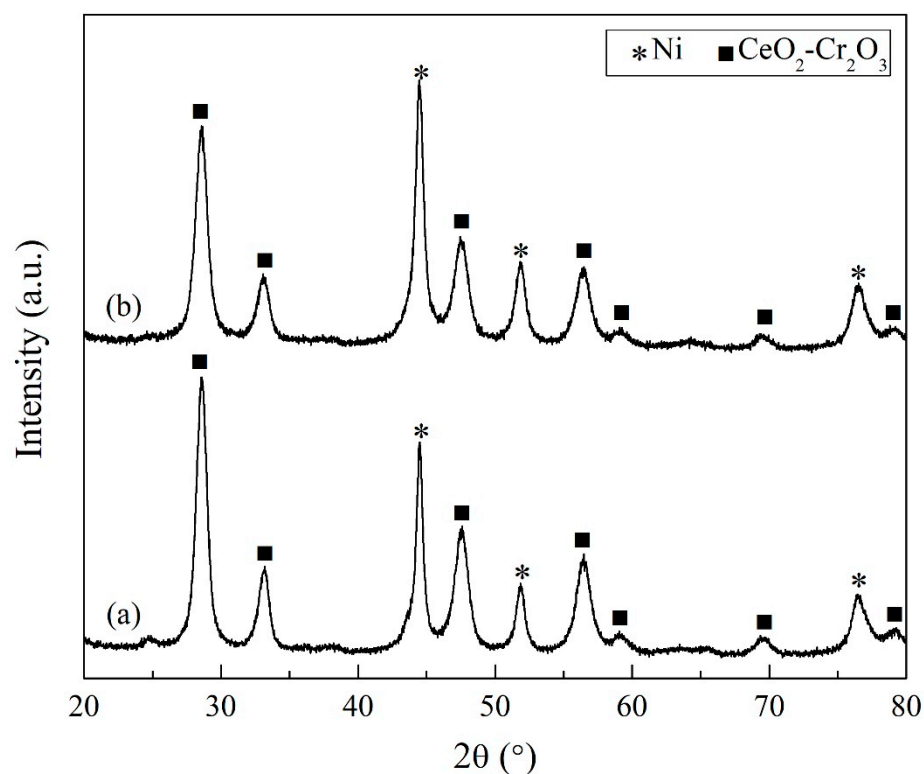


Figure 7. XRD patterns of 40%wt. NiO/CeO₂-Cr₂O₃: (a) before reaction and (b) after stability, where Ni (*) and CeO₂-Cr₂O₃ (■) phases.

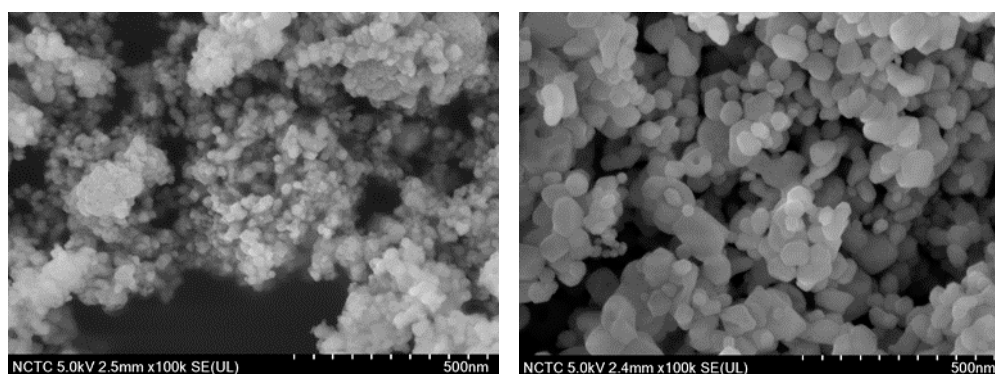


Figure 8. Surface morphology of 40%wt. NiO/CeO₂-Cr₂O₃ at magnification $\times 100,000$: before (Left) reaction and after (Right) stability.

The catalyst performance was compared between this work and other works that researched other catalysts (i.e., 10Ni/CeO₂ [42], 10Ni/CeO₂-ZrO₂ (CZ) [19], 15Ni/CZ, 15Ni-3Fe/CZ, 15Ni-3Co/CZ [42], 40Ni/CZ [3], 15Ni-2Ce/Al₂O₃ [50], 5Ni/CZ [51], 20Ni/Al₂O₃ [52], and 40Ni-5Ce/Al₂O₃ [47]); as shown in Figure 9. Ni/CeO₂-Cr₂O₃ catalyst can be deemed as a superior catalyst due to its high catalytic activity ($Y_{\text{CH}_4} > 95\%$ zone) at low operating temperatures.

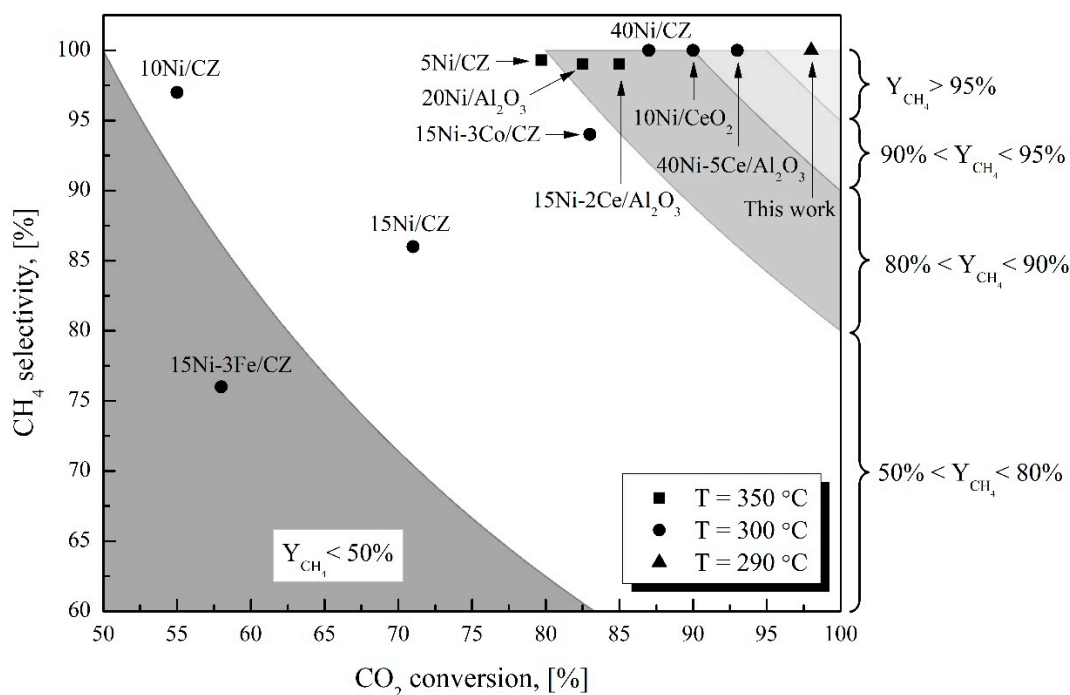


Figure 9. The summaries of the catalytic performances toward CO₂ methanation over various catalysts at H₂/CO₂ = 4:1.

4. Conclusions

The screening of monometallic catalysts (i.e., Ni, Fe and Co) doped on CeO₂-Cr₂O₃ support was studied in a milli-packed bed reactor. All the catalysts were prepared using one-pot hydrolysis. Ni was proven to be the most effective dopant. The amount of Ni loading was found optimal at 40% by weight, giving CO₂ conversion of 98.7% and CH₄ selectivity of 100% at a relatively low temperature of 290 °C. At temperatures of 200 to 350 °C, the reaction was kinetically driven by the higher operating temperature. However, thermodynamic limitation took place at temperatures higher than 350 °C where a drop in catalytic performance was observed. The catalyst was also stable during 50 h time on stream experiment. Ni-CeO₂/Cr₂O₃ was proven to be one of the highest potential catalysts for the CO₂ hydrogenation process of CH₄ production.

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Conflicts of Interest: The authors declare no conflict of interest.

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