Natural Kaolin-Based Ni Catalysts for CO₂ Methanation: On the Effect of Ce Enhancement and Microwave-Assisted Hydrothermal Synthesis

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ABSTRACT: Natural kaolin-based Ni catalysts have been developed for low-temperature CO₂ methanation. The catalysts were prepared via a one-step co-impregnation of Ni and Ce onto a natural kaolin-derived metakaolin using a microwave-assisted hydrothermal method as an acid-/base-free synthesis method. The influences of microwave irradiation and Ce promotion on the catalytic enhancement including the CO₂ conversion, CH₄ selectivity, and CH₄ yield were experimentally investigated by a catalytic test of as-prepared catalysts in a fixed-bed tubular reactor. The relationship between the catalyst properties and its methanation activities was revealed by various characterization techniques including X-ray fluorescence, X-ray diffraction, Brunauer–Emmett–Teller, scanning electron microscopy, selected area electron diffraction, transmission electron microscopy, elemental mapping, H₂ temperature-programmed reduction, and X-ray absorption near-edge structure analyses. Among the two enhancement methods, microwave and Ce promotion, the microwave-assisted synthesis could produce a catalyst containing highly dispersed Ni particles with a smaller Ni crystallite size and higher catalyst reducibility, resulting in a higher CO₂ conversion from 1.6 to 7.5% and a better CH₄ selectivity from 76.3 to 79.9% at 300 °C. Meanwhile, the enhancement by Ce addition exhibited a great improvement on the catalyst activities. It was experimentally found that the CO₂ conversion increased approximately 7-fold from 7.5 to 52.9%, while the CH₄ selectivity significantly improved from 79.9 to 98.0% at 300 °C. Though the microwave-assisted synthesis could further improve the catalyst activities of Ce-promoted catalysts, the Ce addition exhibited a more prominent impact than the microwave enhancement. Cerium oxide (CeO₂) improved the catalyst activities through mechanisms of higher CO₂ adsorption capacity with its basic sites and the unique structure of CeO₂ with a reversible valence change of Ce⁴⁺ and Ce³⁺ and high oxygen vacancies. However, it was found that the catalyst prepared by microwave-assisted synthesis and Ce promotion proved to be the optimum catalyst in this study. Therefore, the present work demonstrated the potential to synthesize a nickel-based catalyst with improved catalytic activities by adding a small amount of Ce as a catalytic promoter and employing microwave irradiation for improving the Ni dispersion.

1. INTRODUCTION

Climate change and global warming as important threats to the human society are closely associated with energy consumption and greenhouse gas (GHG) emissions. Carbon dioxide (CO₂) as the primary GHG (~80%) is mainly emitted by human activities from various sectors such as electricity and heat, transport, industrial, residential, and other sectors. The combustion of fossil fuels such as coal, natural gas (NG), and petroleum oil for energy supply is the main activity that emits CO₂ to the atmosphere. In addition, billion tons of CO₂ emissions are likely increased every year because of the ever-increasing energy consumption. Many research attempts have been dedicated to developing efficient processes to reduce CO₂ emissions by the utilization of captured CO₂ as a feedstock for the production of commodity chemicals and fuels. Nowadays, only a few commercial processes that involve the conversion of CO₂ into value-added chemicals...
exist, for example, processes for production of salicylic acid, urea, and cyclic carbonates.\textsuperscript{11,12} Emerging technologies for CO\textsubscript{2} conversion into commodity chemicals such as dimethyl ether,\textsuperscript{13} formic acid,\textsuperscript{14} carbon monoxide,\textsuperscript{15} ethylene,\textsuperscript{16} dimethylcarbonate, diphenylcarbonate,\textsuperscript{17} polymers (polycarbonates and polyurethanes),\textsuperscript{18} carboxylic acid,\textsuperscript{19} and others have been introduced.\textsuperscript{12,20} However, CO\textsubscript{2} recycling into fuels such as methanol, ethanol, and methane would have a meaningful impact on the reduction of CO\textsubscript{2} emissions.\textsuperscript{21} The synthetic fuels from CO\textsubscript{2} are expected to play a major role in CO\textsubscript{2} emission management strategies due to (i) the world fuel market which is 2 orders of magnitude larger than that of chemicals and (ii) CO\textsubscript{2} emissions mainly being associated with the energy consumption.\textsuperscript{21} Recently, it has been reported that the utilization of NG for heating, electricity generation, and as a chemical feedstock accounts for 20 wt % of global CO\textsubscript{2} emissions.\textsuperscript{22} In addition, the demand of NG is forecasted to increase, while the fossil fuel resources are projected to decline in the near future. Therefore, a synthetic NG (SNG) from a non-fossil-based and sustainable source such as CO\textsubscript{2} is promising in order to meet the ever-growing demand of the market which is 2 orders of magnitude larger than that of chemicals and (ii) CO\textsubscript{2} emissions mainly being associated with the energy consumption.\textsuperscript{21} The SNG production from CO\textsubscript{2} is associated with catalytic hydrogenation of CO\textsubscript{2} into CH\textsubscript{4}, the so-called CO\textsubscript{2} methanation or Sabatier reaction, as shown in eq 1.

\[
\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \\
\Delta H_{298 K}^\circ = -165.15 \text{ kJ mol}^{-1}
\]  

(1)

The reaction requires a highly active catalyst with excellent stability to achieve an acceptably high rate, allowing the methanation to be a viable process. Recently, many researchers have engineered metal-based catalysts with enhanced catalytic activity/performance for the CO\textsubscript{2} methanation process with different aspects such as powerful CO\textsubscript{2} methanation and auto-methanation.\textsuperscript{23–26} Though noble metals such as Ru, Pt, Pd, Re, and Rh are highly active for CO\textsubscript{2} methanation, transition metals such as Ni, Fe, and Co have been widely investigated due to their low price for commercial-scale processes. Among different transition metals, it is reported that Ni-based catalysts exhibit a high activity with the highest CH\textsubscript{4} selectivity for CO\textsubscript{2} methanation.\textsuperscript{27} In particular, nickel is a versatile metal that has been widely used as a hydrogenation catalyst for a number of reactions such as hydrogenation, reforming, gasification, and pyrolysis.\textsuperscript{31–33} In addition, it is reported that the catalytic efficiency of the Ni-based catalyst strongly depends on the support properties.\textsuperscript{34} The catalyst supports provide the huge differences in the metal-support interaction as well as the degree of metal dispersion. In addition, the chemical properties of the support materials such as acidity and basicity can influence the CO\textsubscript{2} adsorption capacity. Moreover, it was recently reported that the surface properties of the support such as oxygen vacancies could greatly enhance the catalyst activity on CO\textsubscript{2} methanation, especially at low temperature.\textsuperscript{35} Generally, the catalyst supports with a large surface area and preferable properties such as SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2}, ZrO\textsubscript{2}, CeO\textsubscript{2}−ZrO\textsubscript{2},\textsuperscript{36–41} and zeolites\textsuperscript{36,41,42} have been widely investigated for CO\textsubscript{2} methanation. These catalyst supports are prepared from pure chemicals. To introduce an option of material selection for catalysis application, natural materials provide advantages of being cost-effective, environment-friendly, and sustainable resources. Natural materials such as hydrotalcite, clay, kaolin, and dolomite have been widely investigated for use as catalyst supports.\textsuperscript{43} As a group of natural clays, kaolin is one of the promising natural materials. Kakavandi et al.\textsuperscript{44} reported the successful use of kaolin as a catalyst support for degradation of organic contaminants in the wastewater treatment. The commercial-scale utilization of kaolin as a catalyst support has been patented by SABIC Global Technologies for the process of syngas production.\textsuperscript{35} Ibrahim et al.\textsuperscript{46} studied the kaolin-supported Ni catalysts for dry methane reforming. In addition, the study reported that raw clay minerals such as kaolinite [Al\textsubscript{4}Si\textsubscript{2}O\textsubscript{5}(OH)\textsubscript{4}], bentonite (bp 381.8 °C), montmorillonite (Al\textsubscript{2}H\textsubscript{2}O\textsubscript{12}Si\textsubscript{4}), sepiolite [Ca\textsubscript{2}O\textsubscript{25}(Mg,Fe)\textsubscript{2}(OH)\textsubscript{2}·n\textsubscript{2}H\textsubscript{2}O], and palygorskite [(Mg,Al)\textsubscript{2}Si\textsubscript{4}O\textsubscript{10}·4] could show a CO\textsubscript{2} adsorption capacity that would be beneficial for CO\textsubscript{2} methanation.\textsuperscript{47} Among the mentioned natural materials, kaolin is promising for the CO\textsubscript{2} methanation reaction due to its higher Al\textsubscript{2}O\textsubscript{3} content (Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} ~ 1). When the promoter is cerium oxide (CeO\textsubscript{2}), the Al\textsubscript{2}O\textsubscript{3}−CeO\textsubscript{2} interaction provides a better redox property and excellent thermal stability of the catalyst.\textsuperscript{38–40} The direct use of kaolin as a support material for CO\textsubscript{2} methanation is rarely studied due to its low surface area and acidic surface. It is usually mentioned that in the state-of-the-art heterogeneous catalysis, the physicochemical property, as well as catalytic performance, of catalyst materials is greatly affected by the preparation method. There are many preparation methods for depositing the active phase metal on the support material to provide high metal dispersion, including impregnation, co-precipitation, sol-gel, hydrothermal synthesis, and so forth.\textsuperscript{51–54} Recently, the microwave-assisted hydrothermal method has received great attention and been widely used for either the chemical reaction or synthesis of nanomaterials with smaller sizes and a uniform structure.\textsuperscript{55–57} This method provides rapid and uniform heating by wave irradiation compared to the conventional hydrothermal route which relies on conduction and convection.\textsuperscript{58} Thus, the microwave heating is a wise option for controlling the particle size and crystalline phase, as well as enhancing the mesoporosity in the synthesis of the nanostructure material. Compared with the traditional hydrothermal method, the microwave hydrothermal method has the characteristics of a fast heating speed, sensitive reaction, and a uniform heating system so that it can rapidly prepare nanoparticles (NPs) with a narrow particle size distribution and uniform morphology.\textsuperscript{59} The uniform particles with nano-scale sizes result in a unique property for catalytic application.\textsuperscript{60} In addition, microwave irradiation has a short heat treatment time and low temperature, making possible its use in large-scale industrial production application.\textsuperscript{59} Recently, Kim et al.\textsuperscript{61} synthesized the catalyst with ruthenium oxide NPs on carbon nanotubes (CNTs) using a microwave digestion system. They reported that the microwave conditions of 1600 W at 200 °C can obtain RuO\textsubscript{2} particles dispersed uniformly over CNTs in only 2 min. Song et al.\textsuperscript{62} examined Ni/Al\textsubscript{2}O\textsubscript{3} prepared by the microwave method compared with that by the conventional impregnation method. The catalyst was prepared by filling the solution in an autoclave with a microwave at 150 °C for 15 min. For the CO\textsubscript{2} methanation, the CO\textsubscript{2} conversion over Ni/Al\textsubscript{2}O\textsubscript{3}−M was higher than that over Ni/Al\textsubscript{2}O\textsubscript{3}−C at the same amount of Ni loading because the Ni species were highly dispersed. Therefore, the microwave technique is selected as an efficient route for obtaining a short reaction time and high dispersion of metal particles on supports.\textsuperscript{52–64}
Recently, the excellent catalytic enhancement of CeO$_2$ in CO$_2$ methanation has been reported.$^{23,35,58,65}$ CeO$_2$ has a number of properties that can be advantageous for the reaction including (i) high oxygen storage capacity,$^{66}$ (ii) excellent redox properties (Ce$^{4+}$/Ce$^{3+}$) with improved metal dispersion and suppressed carbon deposition through carbon oxidation reactions, (iii) strong metal–support interaction (SMSI) that prevents Ni sintering, and (iv) increased basicity for higher CO$_2$ adsorption.$^{67}$ One drawback is that cerium oxide suffers from limited thermal stability at elevated reaction temperatures.$^{68}$ The incorporation of CeO$_2$ with Al$_2$O$_3$ in a Ni-based catalyst leads to a better catalytic activity and higher stability due to the presence of CeO$_2$ species, which helps the adsorption and/or activation of CO$_2$ molecules by high oxygen vacancies,$^{68}$ while the CeO$_2$–Al$_2$O$_3$ interaction increases the catalyst stability.

In this study, the Ni-based catalysts were prepared from natural kaolin. As the catalyst support, kaolin was calcined to metakaolin (MTK). The catalytic enhancements are (i) Ce addition and (ii) microwave-assisted synthesis. The effects of microwave irradiation on the catalyst activity were experimentally investigated. The Ni-based catalysts prepared by the microwave-assisted method were compared to the catalyst prepared by the conventional hydrothermal method. A high Ni loading of 30 wt % was used to discover the loading capability on low-surface-area MTK by means of microwave assistance. The characterization of as-prepared catalysts was performed to understand the relationship between the catalyst activities and the physicochemical properties of the catalyst.

2. RESULTS AND DISCUSSION

2.1. Composition of Kaolin and Metakaolin. Table 1 lists the mineralogical compositions of natural kaolin and metakaolin.

| compositions     | content (wt %)$^a$ | kaolin | metakaolin$^b$ |
|------------------|--------------------|--------|----------------|
| SiO$_2$          | 52.8               | 52.7   |
| Al$_2$O$_3$      | 41.9               |        | 43.2           |
| K$_2$O           | 2.56               |        | 2.39           |
| Fe$_2$O$_3$      | 1.53               |        | 1.45           |
| Na$_2$O          | 0.902              |        |
| MnO              | 0.119              |        | 0.105          |
| MgO              |                    |        | 0.0823         |
| Cl               | 0.0496             |        | 0.0269         |
| SO$_3$           | 0.0456             |        |
| Rb$_2$O          | 0.0449             |        | 0.0399         |

$^a$Compositions determined by XRF. $^b$Metakaolin obtained by calcination of natural kaolin at 650 °C, 2 h.

Metakaolin. X-ray fluorescence (XRF) analysis shows that natural kaolin is mainly composed of SiO$_2$ and Al$_2$O$_3$ with the content of 52.8 and 41.9 wt %, respectively. The impurities are K$_2$O, Fe$_2$O$_3$, Na$_2$O, MnO, Cl, SO$_3$, and Rb$_2$O with the total content of less than 6 wt %. The presence of iron oxide (Fe$_2$O$_3$) is responsible for the typical orange color of natural kaolin.$^{69}$ The presence of Fe$_2$O$_3$ would be beneficial for CO$_2$ methanation as it can catalyze the reaction.$^{70}$ The SiO$_2$/Al$_2$O$_3$ ratio of kaolin in this study is 1.26, which closely corresponds to the report of Bordeepong et al.$^{69}$ They investigated the five samples of kaolin from Ranong, Thailand, with the SiO$_2$/Al$_2$O$_3$ ratio ranging between 1.27 and 1.42. Basically, the SiO$_2$/Al$_2$O$_3$ ratio ranging from 1 to 2 indicates that these two dominant components of kaolin are mixed in a 1:1 ratio with 2:1 dioctahedral phyllosilicates, close to the theoretical ratio of pure kaolinite.$^{71}$ However, the SiO$_2$/Al$_2$O$_3$ ratio of kaolin in this study is slightly higher than 1.0, which is due to the presence of quartz.$^{72}$ In nature, kaolin is a rock that is rich in kaolinite with a chemical structure of Al$_2$Si$_2$O$_5$(OH)$_4$ as well as impurities. The kaolinite contains layers of silicate mineral, with one tetrahedral sheet of silica (SiO$_4$) linked through oxygen atoms to one octahedral sheet of alumina (AlO$_6$).$^{72,73}$ Therefore, before its use as a catalyst support, kaolin is generally calcined to form metakaolin, an amorphous phase of kaolin with less impurities.$^{74}$ According to XRF results in Table 1, the main components of metakaolin are SiO$_2$ and Al$_2$O$_3$ with the content of 52.7 and 43.2 wt %, respectively. The impurities are K$_2$O, Fe$_2$O$_3$, MnO, MgO, Cl, and Rb$_2$O. Notably, the content of impurities was slightly reduced after the calcination process. When compared to the composition of kaolin, it was, however, found that the main composition of metakaolin was unchanged after the calcination process, though the phase and structure were changed. In this study, the observed compositions of both kaolin and metakaolin corresponded well with the literature studies.$^{69,75}$ Adekola et al.$^{75}$ reported the mineralogical compositions of raw kaolin collected from Isale Koko, Ilorin, North Central Nigeria, containing SiO$_2$ and Al$_2$O$_3$ with the content of 52.0 and 43.3 wt %, respectively.

2.2. Morphologies of Kaolin and Metakaolin. Typical morphologies of kaolin and metakaolin were revealed by scanning electron microscopy (SEM), as shown in Figure 1. At a low magnification observation (1000×), kaolin showed agglomerates with an irregular shape. The particle size of bulk kaolin was broadly distributed within a range from 10 to 25 μm. However, at a higher magnification (5000×), it was found that the agglomerate particle comprises a number of thin platelets with a stacking pattern. Other morphologies such as...
presence of quartz, which is highly crystalline SiO$_2$, according to JCPDS card no. 5-0490. In general, natural kaolin comprises the analysis of the textural property analyzed by the N$_2$ sorption measurement, indicating the low Brunauer–Emmett–Teller (BET) surface area.

Figure 2 illustrates the morphology of metakaolin obtained by transmission electron microscopy (TEM). The TEM images elucidate the internal structure of metakaolin as well as the surface morphology. The plate-like particles can be seen, while the layers are likely forming stacks of platelets. The internal structure exhibited a homogeneous texture without any encapsulation or core–shell structure. In addition, metakaolin has a smooth surface, similar to the kaolin surface that is observed by SEM. It was implied that the calcination had generated no further porosity in the metakaolin structure.

2.3. Crystallinity of Kaolin and Metakaolin. Figure 3 displays the X-ray diffraction (XRD) patterns of kaolin and metakaolin recorded from 2$\theta$ = 10 to 90$^\circ$. XRD analysis was used for the determination of phase transformation of kaolin into metakaolin. For the kaolin sample, the presence of kaolinite was indicated by the characteristic diffraction peaks at 2$\theta$ = 12.3, 19.8, 20.2, 20.8, 24.8, 34.9, 38.5, and 55.0$^\circ$.\cite{76,77} Meanwhile, the diffraction peak at 2$\theta$ = 26.6$^\circ$ evidenced the presence of quartz, which is highly crystalline SiO$_2$, according to JCPDS card no. 5-0490. In general, natural kaolin comprises hydrate aluminosilicate with the chemical formula Si$_2$Al$_2$O$_4$(OH)$_4$. By calcination, kaolin is transformed into metakaolin with the chemical formula Al$_2$O$_3$·2SiO$_2$. The process of kaolin calcination is known as dehydroxylation, as shown in eq 2.

$$\text{Si}_2\text{Al}_2\text{O}_4(\text{OH})_4 \rightarrow \text{Al}_2\text{O}_3\cdot2\text{SiO}_2 + \text{2H}_2\text{O}$$ \hspace{1cm} (2)

During the dehydroxylation, the hydroxyl groups are removed from the kaolin structure, releasing water molecules.\cite{78} This also causes a structural transformation (or structural collapse) of the crystalline kaolinite structure into the amorphous phase of metakaolin. Therefore, the diffraction peak of metakaolin shows a broad peak at around 2$\theta$ = 15–35$^\circ$, which confirms the presence of the amorphous phase. The amorphous phase of metakaolin is considered to have higher reactivity than crystalline kaolinite. The higher reactivity of metakaolin would be beneficial for depositing active metals and promoters onto the surface. It was confirmed that the calcination process in this study can completely transform kaolin into metakaolin.\cite{79,80}

2.4. Textural Properties of Catalysts. Textural properties of catalysts including the isotherm type, BET surface area, pore volume, and average pore size were examined by N$_2$ sorption measurement. The sorption isotherms and corresponding pore size distributions of calcined catalysts prepared by the conventional hydrothermal and microwaved-assisted methods for Ce-promoted and unpromoted cases are shown in Figure 4.

According to the IUPAC classification, all of the isotherms of 30Ni/MTK_C, 30Ni/MTK_M, 30Ni–20Ce/MTK_C and 30Ni–20Ce/MTK_M catalysts belong to a typical type IV isotherm with an H3 hysteresis loop. The type IV isotherm indicates the characteristics of mesoporous materials, while the H3 hysteresis loop corresponds to the wedge-shaped pores formed by the stacking of flaky particles.\cite{81} In addition, all of the catalysts exhibited the adsorption–desorption hysteresis loop at a relative pressure of $p/p_0 = 0.45–0.99$, demonstrating that the catalysts contain mesopores with a wide range of pore sizes. In addition, the pore size distribution shows a broad distribution from 1 to 200 nm. For unpromoted catalysts, although the peak of the mesopore is located at 30 to 40 nm, the macropore comprises a majority of the adsorption volume. Meanwhile, the Ce-promoted catalysts had a bimodal pore size distribution at 2 and 30 nm. These two peaks of distribution would be attributed to the porous structure of CeO$_2$ added to the catalysts. Table 2 lists the textural properties of as-prepared catalysts such as the specific BET surface area ($S_{\text{BET}}$), pore volume ($V_{\text{pore}}$), and average pore size ($D_{\text{p}}$).

The surface area of the catalyst prepared by the microwaved-assisted method was higher than that of catalysts prepared by the conventional method, implying that Ni particles of the catalysts prepared by the conventional method were agglomerated, leading to the decreased surface area. Furthermore, the surface area of the catalysts promoted with Ce was compared with the unpromoted Ni/MTK catalyst. The addition of Ce slightly increased the surface area of catalysts, from 17.68 to 23.83 m$^2\cdot$g$^{-1}$ for the conventional method and from 24.88 to 31.18 m$^2\cdot$g$^{-1}$ for the microwave-assisted method. This result corresponds to the previous study. Wang et al.\cite{58} found an increase in the surface area by adding Ce to the catalyst. This is due to the formation of the CeO$_2$ porous structure.
2.5. Crystallinity of Catalysts. The XRD patterns of all calcined catalysts are given in Figure 5. The characteristic diffraction peaks at \( 2\theta = 37.3, 43.2, 62.9, 75.3, \) and 79.4° can be assigned to cubic NiO according to JCPDS 47-1049, with the various diffraction planes of (111), (200), (220), and (222), respectively. Meanwhile, the diffraction peaks at \( 2\theta = 28.7, 33.3, 47.7, \) and 56.6° are assigned to the (111), (200), (220), and (311) planes of CeO\(_2\), respectively, according to JCPDS no. 34-0394. Moreover, the diffraction peak at 26.6° is assigned to quartz which is inherently from metakaolin.

The crystallite sizes of NiO and CeO\(_2\) in the as-prepared catalysts were calculated using the prominent XRD refractions of NiO(200) and CeO\(_2\)(111) planes. The calculation employed Rigaku PDXL software based on a Scherer equation. It was found that the NiO crystallite sizes of 30Ni/MTK_C, 30Ni/MTK_M, 30Ni−20Ce/MTK_C, and 30Ni−20Ce/MTK_M catalysts were 28.8, 24.5, 28.0, and 24.0 nm, respectively. Meanwhile, the CeO\(_2\) crystallite sizes of 30Ni−20Ce/MTK_C and 30Ni−20Ce/MTK_M catalysts were 98.5 and 113.1 nm, respectively. It was implied that the microwave-assisted hydrothermal method can reduce the crystallite size of NiO when compared to the conventional hydrothermal method. However, the crystallite size of CeO\(_2\) by the microwave-assisted method was found to be bigger than that of the conventional hydrothermal method.

2.6. Morphology of Catalysts. The TEM images of 30Ni/MTK_C, 30Ni/MTK_M, 30Ni−20Ce/MTK_C, and 30Ni−20Ce/MTK_M catalysts are presented in Figure 6. As shown in Figure 6, Ni particles, which are represented by dense particles, were apparently dispersed on the surface of the MTK support. Also, it could be seen that the catalysts prepared by the conventional hydrothermal method (30Ni/MTK_C and 30Ni−20Ce/MTK_C) in Figure 6a,c have a very dense agglomeration of Ni particles. In contrast, the catalysts prepared by the microwave-assisted method (30Ni/MTK_M and 30Ni−20Ce/MTK_M) possess highly dispersed Ni particles as shown in Figure 6b,d. The selected area electron diffraction (SEAD) images of all catalysts are revealed in Figure 6e–h. The diffraction pattern confirms the presence of NiO and CeO\(_2\) in the samples. The interplanar distance is 0.20 Å, which corresponds to the NiO(200) plane, while the interplanar distance of 0.31 Å corresponds to the CeO\(_2\)(111) plane. These SEAD results correspond well with the XRD results.

2.7. Metal Dispersion of Catalysts. The element mapping displays the distribution of Ni elements over the MTK support for 30Ni/MTK_C and 30Ni/MTK_M (Figure 7a,b) and the distribution of Ni and Ce elements over the MTK support for 30Ni−20Ce/MTK_C and 30Ni−20Ce/MTK_M (Figure 7c,d). The elemental mapping of Si and Al was also carried out to obtain the area of the MTK support. The red-colored area in Figure 7a–d reveals the presence of Ni particles on the MTK surface, which indicates that Ni particles are mainly anchored on the surface of the MTK support without entering into the internal structure of MTK. These results correspond to the Ni crystallite sizes observed by XRD, which are bigger than the pore size diameter of MTK (Table 2). Additionally, the catalysts with the addition of the Ce promoter, CeO\(_2\), were dispersed outside the pore of the MTK support because the crystallite size is larger than the pore size diameter of MTK.
pore size according to the textural property results. As for the
degree of dispersion, the 30Ni/MTK_M catalyst showed highly
dispersed Ni on MTK when compared to the 30Ni/MTK_C catalyst structure, attributed to the effective assistance
of microwave irradiation. In addition, Ce-promoted catalysts showed uniform incorporation of Ni and Ce. Notably, Ni and Ce of the 30Ni–20Ce/MTK_M catalyst exhibited better uniformity than those of the 30Ni–20Ce/MTK_C catalyst.

2.8. Reducibility of Catalysts. Figure 8 presents H2 temperature-programmed reduction (TPR) profiles of the calcined catalysts prepared by microwave-assisted and conventional hydrothermal methods with Ce-promoted and unpromoted cases. H2-TPR was performed to investigate the reducibility of the catalyst which contains reducible NiO species and partially reducible CeO2 species. As shown in Figure 8, the first reduction peaks at low temperatures of 325–340 °C could be assigned to α-type NiO species, which are free NiO particles reduced into metallic Ni as well as NiO particles with weak interaction with the MTK surface.44 The second peak could be assigned to β-type NiO species with medium interaction with the catalyst support. Meanwhile, the high-temperature peak is assigned to γ-type NiO species which are NiO particles with strong interaction with the support and the stable nickel aluminate phase with the spinel structure (NiAl2O4).45,84

It was found that all of the as-prepared catalysts 30Ni/MTK_C, 30Ni/MTK_M, 30Ni–20Ce/MTK_C, and 30Ni–20Ce/MTK_M contained three types of NiO species, which are α, β, and γ types. Considering the highest reduction peak (β type) of the 30Ni/MTK_M catalyst, the peak was shifted to a lower temperature. This indicates that the NiO species with smaller sizes were highly dispersed on the support, corresponding to the smaller NiO crystallite size determined by XRD analysis. In contrast, the catalysts prepared by the microwave-assisted method with Ce added resulted in the peak shifting to a higher temperature. It indicates that the interaction between the NiO species and MTK support and/or CeO2 was greatly increased. The co-precipitation of Ni and Ce gave a chance to form a strong interaction structure that incorporated NiO and CeO2 during the calcination step. There is a study that reported that Ni favorably interacted with Ce species.46 Moreover, the addition of Ce into the Al2O3–SiO2 support can increase the CO2 adsorption capacity.67 Adsorbed CO2 is further activated on the surface of CeO2 via the partial dissociation of CO2, resulting in CO intermediates for further hydrogenation to methane.67 These properties of CeO2 would improve the activity of the catalyst for CO2 methanation.

Table 3 lists the Ni content, reduction temperature, NiO crystallite size, H2 consumption, and reducibility of catalysts prepared from the microwave-assisted hydrothermal and convention hydrothermal methods for Ce-promoted and unpromoted cases. The actual Ni content determined by XRF was approximately 27 wt % around 3 wt % less than the calculation. All catalysts showed a comparable Ni content. The actual Ni content was used for the calculation of the theoretical H2 consumption. The reducibility is defined as the reduction temperature peak and the percent reducibility calculated from experimental and theoretical values of H2 consumption. It was found that the reduction temperature peaks of 30Ni/MTK_C, 30Ni/MTK_M, 30Ni–20Ce/MTK_C, and 30Ni–20Ce/MTK_M were located at 419, 398, 405, and 425 °C, respectively. The reduction temperature peak indicates the difficulty of reduction of NiO, which is directly associated with the (i) crystallite size of NiO and (ii) degree of Ni interaction with other species. For the unpromoted catalysts, the reduction peaks at higher temperatures (419 and 398 °C) would imply the bigger Ni particles of 30Ni/MTK_C, 30Ni/MTK_M, and 30Ni–20Ce/MTK_M compared to that of 30Ni/MTK_C (NiO = 24.5 nm), which corresponds with the XRD result. For the Ce-promoted catalyst, 30Ni–20Ce/MTK_C showed more distinct peaks of α and β types. The Ce addition to 30Ni–20Ce/MTK_C resulted in slightly smaller NiO (NiO = 28.0 nm) compared to 30Ni/MTK_C (NiO = 28.8 nm). This also shifts the reduction peak from 419 to 405 °C for 30Ni/MTK_C and 30Ni–20Ce/MTK_C, respectively. Interestingly, 30Ni–20Ce/MTK_M showed the highest reduction peak at 425 °C. This would be attributed to the stronger interaction between NiO and CeO2 for microwave synthesis. The microwave irradiation would help incorporate NiO species into the CeO2 structure during the catalyst synthesis. It should be further noted that the α region showed the highest area, compared to others, attributed to the smallest NiO particles (NiO = 24 nm). Without careful analysis, the H2 consumption values from the experiment would be arbitrary. Therefore, it was used for the calculation of percent reducibility based on the actual amount of Ni, which is converted to the theoretical H2 consumption value. For the unpromoted catalysts, the percent reducibility corresponded with the NiO sizes. Similarly, the Ce-promoted catalysts showed a better percent reducibility due to the smaller NiO particles. Moreover, it should be noted that the percent reducibility improved with
2.9. Oxidation State of Catalysts. The X-ray absorption near-edge structure (XANES) spectra at the Ni K-edge and the first derivative of $\mu(E)$ of 30Ni/MTK_C and 30Ni/MTK_M catalysts compared to the Ni foil and NiO standard are given in Figure 9a. Both catalysts were calcined in air at 500 °C for 3 h. The calcined catalysts displayed spectra that resemble that of NiO, indicating the formation of Ni$^{2+}$ species. The derivative plot reveals two maximum peaks around 8332 and 8343 eV. The standard Ni foil has the first maximum value at 8332 eV, while standard NiO and both calcined catalysts showed the same highest value at 8343 eV. It could be seen that the presence of NiO in 30Ni/MTK_C and 30Ni/MTK_M catalysts were confirmed. Moreover, linear combination analysis which gives quantitative details of the Ni phase of both calcined catalysts reveals the amount of 100% NiO without Ni$_2$O, representing that NiO of both catalysts was more easily reduced to the Ni metallic form. Figure 9b shows the XANES spectra at the Ni K-edge and the first derivative of $\mu(E)$ of reduced 30Ni/MTK_C and reacted 30Ni/MTK_M catalysts compared to the Ni foil and NiO standard. It was observed that the reduced catalysts showed spectra that resemble that of Ni foil, indicating the formation of Ni$^{0}$ species.

Table 3. H$_2$ Consumption and Reducibility of Calcined Catalysts

| catalysts          | Ni (wt %)$^a$ | $T_{\beta}$ (°C)$^b$ | $D_{NiO}$ (nm)$^c$ | H$_2$ consumption (mmol·g$^{-1}$) | reducibility (%) |
|--------------------|---------------|----------------------|---------------------|----------------------------------|-----------------|
|                    |               |                      |                     | experiment$^a$ | theoretical$^a$ |               |
| 30Ni/MTK_C         | 27.68         | 419                  | 28.8                | 3.485               | 4.717           | 73.9           |
| 30Ni/MTK_M         | 26.89         | 398                  | 24.5                | 3.605               | 4.582           | 78.7           |
| 30Ni−20Ce/MTK_C    | 27.04         | 405                  | 28.0                | 3.492               | 4.608           | 75.8           |
| 30Ni−20Ce/MTK_M    | 26.57         | 425                  | 24.0                | 3.689               | 4.528           | 81.5           |

$^a$Actual Ni content by XRF analysis. $^b$Reduction temperature of $\beta$-peak Ni. $^c$NiO crystallite size by XRD. $^d$H$_2$ consumption by H$_2$-TPR. $^e$Theoretical H$_2$ consumption based on the actual Ni content.
found that the spent catalyst contained a metallic form of Ni, similar to the reduced catalyst.

2.10. Catalytic Activity of Catalysts. Figure 10 shows the catalytic activities including the CO2 conversion ($X_{CO2}$), CH4 selectivity ($S_{CH4}$), and CH4 yield ($Y_{CH4}$) of all four catalysts 30Ni/MTK_C, 30Ni/MTK_M, 30Ni−20Ce/MTK_C, and 30Ni−20Ce/MTK_M for CO2 methanation under a molar ratio of CO2/H2/He = 1/4/5 with a total flow of 70 mL·min$^{-1}$ through a catalyst bed (powder form) of 100 mg corresponding to a weight hourly space velocity (WHSV) of 42,000 mL·g$^{-1}$·h$^{-1}$ in the temperature range 225−500 °C. For the unpromoted catalysts (30Ni/MTK_C, 30Ni/MTK_M), it was apparent that the catalyst synthesized by the microwave-assisted method exhibited higher catalytic activities for both CO2 conversion and CH4 selectivity at all investigated reaction temperatures from 225 to 500 °C. This corresponds with our previous work, demonstrating that the microwave-assisted synthesis could increase the catalyst activities, even the high Ni content of 30 wt % due to the smaller NiO crystallite size.110 The temperature at 50% conversion ($T_{50\%}$) is usually determined to indicate the catalyst activity. In this study, the CO2 conversion of 30Ni/MTK_M and 30Ni/MTK_C reached 50% conversion at 396 and 408 °C, respectively. This indicated that microwave irradiation can enhance the catalyst activity, especially at the low-temperature range for CO2 methanation. The higher catalytic activity of the catalyst prepared by the microwave-assisted method was due to the highly dispersed Ni particles on the MTK support with a smaller Ni crystallite size, compared with that of the catalyst synthesized by the conventional hydrothermal method. The smaller Ni particles dispersed on MTK provide the higher Ni reducibility. This reason was confirmed by XRD and H2-TPR results as previously described. The heat transfer mechanism of the microwave progresses rapidly and uniformly compared to the conventional heating.86 For conventional heating, the heat is transferred through the surface of the container. After that, the hot surface may lead to local overheating. However, microwave heating transfers heat directly to substances by wave irradiation.

For the Ce-promoted catalysts 30Ni−20Ce/MTK_M and 30Ni−20Ce/MTK_M, the CO2 conversions of both catalysts were relatively similar at the high temperature of 350−500 °C. The effect of the microwave was not clearly observed at such high temperatures. However, the effect of the microwave was found at the low temperature of 225−300 °C. The microwave can show an improved catalytic activity compared to the conventional hydrothermal method. Meanwhile, the CH4 selectivities of both catalysts were identical at all investigated temperatures due to the excellent Ce promoter. It confirms that Ce addition greatly enhanced the product selectivity toward CH4 formation. When compared to the unpromoted catalysts, the catalysts with Ce addition showed a great improvement with either the microwave-assisted method or the conventional hydrothermal method. This emphasizes the importance of Ce addition compared to the microwave enhancement. Figure 10b presents the CH4 yields of all prepared catalysts. The values correspond to the CO2 conversion and CH4 selectivity. The effect of microwave
irradiation was investigated in both cases of unpromoted and Ce-promoted catalysts. From Figure 10, it is concluded that the microwave-assisted synthesis improved the catalytic performance in terms of CO2 conversion and CH4 selectivity. However, the Ce addition exhibited a profound effect on the catalytic enhancement compared to the microwave-assisted synthesis. The Ce addition provides CeO2 with a higher CO2 adsorption capacity. Adsorbed CO2 can be further activated to form the intermediate species by oxygen vacancies on the surface of CeO2. The optimum catalyst in this study was 30Ni–20Ce/MTK_M.

Table 4 lists the selected physicochemical properties of the catalysts including specific surface area ($S_{BET}$), NiO crystallite sizes ($D_{NiO}$), and % reducibility to reveal the relationship with the methane production yield ($Y_{CH4}$) and reaction rates of CO2 consumption ($r_m$ and $r_r$). The CH4 yields of all catalysts corresponded with the order of catalyst activity that is determined by the CO2 conversion. It was found that the specific surface area corresponded with the smaller crystallite size of NiO, resulting in the better % reducibility. Therefore, the reaction rates with respect to the mass and surface had similar trends. The increase in the surface area played a minor role in the catalytic enhancement. Meanwhile, the crystallite size and % reducibility were found to be directly related to the catalytic activity. It was implied that the microwave-assisted method can improve the Ni dispersion by reducing the Ni crystallite size. Furthermore, the higher catalytic performance of Ni-based catalysts prepared by the microwave method and Ce promotion can be observed from the mass reaction rates and surface reaction rates.

2.11. Kinetic Parameters of Catalysts. The kinetic parameters of all prepared catalysts were evaluated using data of the CO2 methanation test in the temperature range 250–400 °C. The catalytic tests of these catalysts were carried out under the same reaction conditions. The Arrhenius plot which is the logarithm of the rate constant $k$ as a function of $1/T$ is presented in Figure 11. The activation energy ($E_a$) was obtained using linear regression of plotted data. The activation energy was calculated from the slope of the fitted lines of rate constants. It was found that the activation energies of the catalysts were in the order 30Ni–20Ce/MTK_M (55.1 kJ/mol) < 30Ni–20Ce/MTK_C (67.9 kJ/mol) < 30Ni/MTK_M (83.8 kJ/mol) < 30Ni/MTK_C (116.8 kJ/mol). The 30Ni–20Ce/MTK_M catalyst showed the lowest activation energy compared to the other catalysts. It indicates that the 30Ni–20Ce/MTK_M catalyst had the highest catalytic performance. Furthermore, the addition of 20 wt % CeO2 resulted in enhanced catalytic efficiency of the catalysts prepared by both methods. It was due to the properties of CeO2, which can facilitate the formation of oxygen vacancies on the CeO2 surface, resulting in a higher rate of CO2 activation. In addition, the values of activation energy in this study are comparable with the activation energies of Ni/CeO2 catalysts reported in the literature with $E_a = 94.9–106.0$ kJ/mol.

2.12. Stability of Catalysts. Figure 12 presents the stability of the optimum catalyst in this study: 30Ni–20Ce/MTK_M. The test was performed at 350 °C over 100 mg of the catalyst powder with a feed gas ratio of CO2/H2/He = 1/4/5 (molar ratio) at a total flow rate of 70 mL min$^{-1}$ corresponding to a WHSV of 42,000 mL g$^{-1}$ h$^{-1}$. To determine the catalyst stability, the catalytic activities including CO2 conversion, CH4 selectivity, and CO selectivity were continuously observed over the time on stream value of 48 h. It was found that the catalyst proved to be highly stable during the test for 48 h. More specifically, the initial CO2 conversion started at 61.2%, and then, it turned to 59.7% after 48 h. In another word, the drop in the CO2 conversion was less than 2%. Meanwhile, the initial CH4 selectivity was at 98.1%. Surprisingly, the CH4 selectivity could be maintained at around 97.5% during the test for 48 h.
98.0% for 48 h. It could be said that the drop in CH₄ selectivity was negligible. Typically, the deactivation of the methanation catalyst was due to Ni sintering and carbon deposition. The sintering mechanism results in the lower activity due to the bigger Ni particles with a lower active surface area. It is due to the hotspot created by the accumulation of highly exothermic heat from the reaction. It is reported that the high Ni particle dispersion with a smaller size reduces the metal sintering. In other word, the microwave-assisted synthesis can help increase the catalyst stability by high dispersion of Ni on MTK. Meanwhile, the carbon deposition is associated with the acidity on the catalyst surface. It is known that Al₂O₃ has an acidic surface, resulting in possible carbon deposition with the high-temperature reaction. The addition of a basic material into the catalyst is expected to reduce the carbon deposition. In this study, the high stability of the catalyst would be mainly attributed to the influence of Ce addition. It is reported that CeO₂ can suppress the carbon deposition on the catalyst due to its basicity. Furthermore, the interaction between Ni and Ce would result in SMSI. The SMSI effect can prevent the Ni metal sintering.

2.13. Proposed Mechanism. Figure 13 depicts the proposed mechanism for the formation of Ni and Ce particles on the MTK support. The catalytic activities in terms of the CH₄ yield \((Y_{\text{CH}_4})\) at 300 °C were compared. Two catalytic enhancement methods: (i) microwave-assisted synthesis and (ii) Ce addition result in four cases of catalysts: 30Ni/MTK_C, 30Ni/MTK_M, 30-20Ce/MTK_C, and 30Ni–20Ce/MTK_M. For the enhancement by microwave-assisted synthesis, the microwave irradiation produces efficient internal heating by direct coupling of microwave energy with the molecules of the solution by high-frequency electromagnetic radiation. The high heating efficiency is caused by the energy of the microwaves directly reaching and being absorbed by the substance. In microwave-assisted heating, the rapid temperature rise facilitates nanomaterial synthesis to form in a homogeneous mixture of the precursor solution. In addition to the increase in the formation rate, the microwave provided uniform heating of the whole solution. This enabled us to obtain a better control of the NPs’ nucleation and growth, directly influencing the particle size distribution. Motshegka et al. reviewed that the microwave-assisted synthesis of the composites allows processes to be completed within a shorter reaction time with uniform and well-dispersed NP formation. Compared to the conventional hydrothermal method, the microwave hydrothermal method supplies heat by not only conduction but also microwaves. On the other hand, the conventional hydrothermal method supplies the heat to the solution via two modes of heat transfer: conduction and convection, which rely on the thermal conductivity of the solution and the movement of the solution, respectively. This heat transfer mechanism results in a slow heating rate as well as the non-uniform temperature of the solution. Consequently, bulky Ni particles are formed, especially at a high Ni loading of 30 wt %. By characterization, smaller Ni particles with better Ni dispersion and a higher surface area for microwave-assisted synthesis \((D_{\text{Ni}} = 24.5 \text{ nm, } S_{\text{BET}} = 24.88 \text{ m}^2/\text{g})\) than those for the conventional hydrothermal method \((D_{\text{Ni}} = 28.8 \text{ nm, } S_{\text{BET}} = 17.68 \text{ m}^2/\text{g})\) were found. As a result, the CH₄ production yield of 30Ni/MTK_M \((Y_{\text{CH}_4} = 6.0\% )\) was higher than that of 30Ni/MTK_C \((Y_{\text{CH}_4} = 1.3\%)\) by almost 5-fold at 300 °C.

For the enhancement by Ce addition, cerium oxide \((\text{CeO}_2)\) is formed on the catalyst surface in contact with Ni particles, as depicted in Figure 13. The advantages of \text{CeO}_2 are the (i) basicity of the surface and (ii) oxygen vacancy. The basicity of \text{CeO}_2 enhances the CO₂ adsorption capacity. It is also reported that the basicity of the catalytic support is beneficial to coke elimination. Meanwhile, the oxygen vacancy can activate adsorbed CO₂ to form CO species. The adsorbed CO species is further hydrogenated to form bidentate formate species. Finally, these intermediates are further hydrogenated to form CH₄. Therefore, the addition of Ce has a great impact on the catalytic enhancement for CO₂ methanation. The activities including CO₂ conversion and CH₄ selectivity were greatly improved. Comparing 30Ni–MTK with 30Ni–20Ce/MTK_C, the CH₄ yield was greatly increased by 36-fold at 300 °C (from 1.3 to 47.8%). In addition, the improvement by the microwave-assisted synthesis was further found in the Ce-promoted catalyst \((30\text{Ni–20Ce/MTK_M})\). The Ni crystallite size and specific surface area of 30Ni–20Ce/MTK_M \((D_{\text{Ni}} = 24.0 \text{ nm, } S_{\text{BET}} = 31.18 \text{ m}^2/\text{g})\) compared to those of 30Ni–20Ce/MTK_C \((D_{\text{Ni}} = 28.0 \text{ nm, } S_{\text{BET}} = 23.83 \text{ m}^2/\text{g})\) were improved. However, the CH₄ yield was slightly increased from 47.8 to 51.9%. It was experimentally found that the Ce addition played a crucial role in the catalytic enhancement. It can be described by the reaction mechanism of CO₂ methanation. Typically, H₂ adsorbs on the Ni surface, while CO₂ preferably adsorbs on the support surface. Subsequently, H₂ is dissociated on the Ni active site to form an adsorbed H atom, while the CO₂ molecule is activated on the support surface. Adsorbed H₂ proceeds via a spillover mechanism to the interface of Ni and the support and/or the support. Finally, the hydrogenation is proceeded until CH₄ is obtained. From this mechanism, it is observed that the H₂ dissociation is not the rate-determining step, while the CO₂ activation exhibits a slower step with a higher energy barrier. \text{CeO}_2 with a highly active oxygen vacancy thus reduces the energy barrier of the reaction. Therefore, Ce addition greatly enhances the catalytic activity of the catalyst.
3. CONCLUSIONS

This study aimed to develop a cost-effective Ni-based catalyst with a high catalytic activity/performance from abundant and inexpensive natural kaolin for the application in a low-temperature CO₂ methanation process. Two enhancement methods including Ce addition and microwave-assisted synthesis have been applied to improve the catalyst activity/performance. Microwave irradiation was found to effectively increase the Ni dispersion on the support, revealed by XRD and H₂-TPR analyses; thus, the high nickel content can be effectively loaded on low-surface-area metakaolin. Compared to the conventional hydrothermal method, the catalyst prepared by the microwave-assisted method exhibited the better catalytic activity for CO₂ methanation in terms of both CO₂ conversion and CH₄ selectivity. However, it was found that the addition of Ce showed profound catalytic enhancement compared to the increased Ni dispersion by the microwave-assisted method. The catalyst promoted by Ce addition exhibited great improvement in both CO₂ conversion and CH₄ selectivity, especially at low temperature. As the excellent catalytic promoter, CeO₂ provided a large CO₂ adsorption value due to its basic surface. Adsorbed CO₂ was easily activated by the oxygen vacancies on the CeO₂ surface. This study demonstrated that the Ce addition combined with microwave-assisted synthesis can provide a promising route for the synthesis of high-catalytic-activity/performance Ni catalysts for a low-temperature CO₂ methanation process.

4. EXPERIMENTAL SECTION

4.1. Materials. Natural kaolin was locally produced in Ranong, Thailand (Mineral Resources Development Co., Ltd.). Kaolin typically contains kaolinite with the chemical formula Al₂O₃·2SiO₂·2H₂O. Before use, kaolin was calcined at 650 °C for 2 h at a heating rate of 10 °C·min⁻¹ to transform kaolin into MTK as well as to remove impurities. The obtained MTK was used as a catalyst support in this study. Nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O) (purity >99.0%, Sigma-Aldrich) and cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O) (purity >98.0%, Sigma-Aldrich) were employed to provide Ni as an active phase metal and Ce as a catalytic promoter. Distilled water was used throughout the catalyst preparation. Ultra-high purity gases including CO₂, H₂, and He (purity >99.9999%, Jantong Co. Ltd.) were used as reactant gases and carrier gas. Quartz wool fiber (OV-3351, Ohio Valley Specialty) was used for immobilization of the catalyst bed in the reactor tube.

4.2. Catalyst Preparation. Catalysts were prepared by one-step co-impregnation of Ni and Ce on metakaolin using the microwave-assisted hydrothermal method. The preparation is free from any precipitating agents. The catalysts synthesized by the conventional hydrothermal method with similar conditions to the microwave-assisted method were prepared for comparison. The synthesis conditions of all catalysts are summarized in Table 5. The Ni metal loading was fixed at 30 wt %, while the Ce promoter amount was set at 20 wt % based on its oxide form (CeO₂). The catalytic enhancement by Ce addition was investigated by comparison with the unpromoted Ni/MTK catalysts in the previous work.¹¹⁰

In brief, the mixture of Ni and Ce nitrate solutions was added dropwise into the MTK powder to form a slurry. The homogeneous slurry was then filled in a Teflon-lined vessel of a commercial microwave digestion system (Multiwave PRO, Specialty) was used for immobilization of the catalyst bed in the reactor tube.

| catalysts¹ | Ni (wt %) | Ce (wt %) | conc.² (mol·L⁻¹) | heating method | ref |
|-----------|-----------|-----------|-------------------|----------------|-----|
| 30Ni/MTK_C | 30        | 0.8       |                   | hot air oven, 220 °C | 110 |
| 30Ni/MTK_M | 30        | 0.8       |                   | microwave, 220 °C | 110 |
| 30Ni–20Ce/MTK_C | 30 | 20       | 0.8               | hot air oven, 220 °C | this work |
| 30Ni–20Ce/MTK_M | 30 | 20       | 0.8               | microwave, 220 °C | this work |

¹MTK = metakaolin derived from natural kaolin. ²Ni loading (metallic Ni). ³Ce loading (CeO₂). ⁴Concentration of Ni and Ce nitrate salts. ⁵Microwave power kept constant at 1200 W, C = conventional hydrothermal method and M = microwave hydrothermal method.

Anton Paar) to provide microwave irradiation treatment. The microwave treatment (denoted as M) was operated at 1200 W, which created a temperature of 220 °C and an autogenous pressure of 60 barg for 2 h digestion time. In the conventional hydrothermal method (denoted as C), the sample was filled in a Teflon-lined autoclave. Then, the autoclave was put in a hot air oven at 220 °C for 2 h with the expected similar pressure developed. After cooling down the autoclaves, water as a solvent was completely removed by evaporation at 80 °C to obtain the dried sample as a powder. In particular, by the slow evaporation, the contents of Ni and Ce load on MTK are controlled. The dried sample was then calcined in air at 500 °C for 3 h at a heating rate of 10 °C·min⁻¹. Finally, the as-prepared catalyst was then kept in a desiccator for further characterization and catalytic testing.

4.3. Catalyst Characterization. The morphology and metal species distribution of the support material and the prepared catalysts were acquired using a field emission scanning electron microscope (HITACHI SU-8010, and JEOL JSM-7610F) and a transmission electron microscope (JEOL/JEM-2100Plus) at 200 kV. The TEM sample was prepared in pure ethanol (99.9% v/v) through ultrasonic washing and carefully dropped on a TEM copper grid. The TEM-equipped energy dispersive spectroscopy was used for elemental mapping to reveal the metal dispersion. The chemical compositions of kaolin, metakaolin, and the prepared catalysts were determined by a micro XRF instrument (Bruker M4 Tornado) with Rh radiation under vacuum conditions. The BET surface area (S_BET), pore volume (V_p), and average pore diameter (D_p) of the catalyst samples were analyzed at −196 °C under a N₂ atmosphere using a porosity analyzer (3Flex, Micromeritics, USA) connected with the degassing equipment (Smart VacPrep, Micromeritics, USA). The sample was degassed at 200 °C for 1 h before the analysis. The crystallinity of the support and prepared catalysts was analyzed by XRD analysis (D8 ADVANCE, Bruker) using Cu Kα radiation at 40 kV and 30 mA, over a 2θ range of 10−90° at a scan speed of 2°·min⁻¹. The crystallite sizes of NiO and CeO₂ in the samples were calculated by Rigaku PDXL software. The reducibility and metal−support interaction were examined by H₂-TPR experiments of the calcined samples (BELCAT II, TCD detector). Prior to the analysis, the residual moisture and volatile species in the calcined samples were removed at 200 °C for 1 h under a He flow rate of 30 cm³·min⁻¹. The H₂ consumption was recorded using a thermal conductivity

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detector (TCD). The H2-TPR profiles were obtained by increasing the temperature from 100 to 900 °C at a heating rate of 10 °C·min⁻¹ under a H2/Ar flow of S/95 (v/v) at a flow rate of 30 cm³·min⁻¹. The ex situ XANES analysis was used to provide further insight into the change in the oxidation states of Ni catalysts. The XANES spectra were investigated at Beamline 8 of the Synchrotron Light Research Institute (SLRI), Thailand, using a Ge(220) monochromator crystal for scanning the photon energy. Photon energy calibration was performed using Ni and NiO with reference K-edge energies of 8332 and 8343 eV, respectively. All of the spectra and linear combination fitting were analyzed by the ATHENA program.

4.4. Measurement of Catalyst Activities. The CO₂ methanation reaction was conducted in a horizontal fixed-bed tubular reactor made of quartz (8 mm Ø i.d. × 600 mm long) as schematically shown in Figure 14. The catalyst powder measuring 100 mg was packed in the middle of the reactor by immobilization with quartz wool. The reactor was heated by the electric furnace equipped with a PID controller and a type-K thermocouple to the desired temperature. Then, the gas mixture at a molar ratio of CO2/ H2/He = 1/4/5 with a total flow rate of 70 mL min⁻¹ was fed into the reactor, corresponding to a WHSV of 42,000 mL g⁻¹ h⁻¹. The reaction test was performed at the setting temperature ranging from 225 to 500 °C at atmospheric pressure. The actual temperature of the reaction was separately measured by using another thermocouple placed at the center of the catalyst bed outside the reactor. At the outlet stream, steam (H₂O) from the reaction was removed by a condenser at 5 °C. The flow rate of the effluent gas with a dry basis was measured by a calibrated soap film meter. The composition of the effluent gas including CO₂, CH₄, and CO was analyzed by a gas chromatograph (GC-8A, TCD, Shimadzu).

4.5. Analysis of Catalytic Activity. CO₂ conversion (XCO₂), CH₄ selectivity (SCH₄), CO selectivity (SCO), and CH₄ yield (YCH₄) were calculated by using eqs 3–6, respectively.

\[
X_{CO_2} (%) = \frac{[CO_2]_{in} \times F_{in} - [CO_2]_{out} \times F_{out}}{[CO_2]_{in} \times F_{in}} \times 100
\]  

\[
S_{CH_4} (%) = \frac{[CH_4]_{out}}{[CO]_{out} + [CH_4]_{out}} \times 100
\]  

\[
S_{CO} (%) = \frac{[CO]_{out}}{[CO]_{out} + [CH_4]_{out}} \times 100
\]  

\[
Y_{CH_4} (%) = \frac{X_{CO_2} \times S_{CH_4}}{100}
\]  

where [i]_{in} and [i]_{out} represent the concentrations of reactants (i = CO₂) or products (i = CO or CH₄) at the inlet and outlet of the reactor, respectively. F_{in} and F_{out} are the total flow rates (mL min⁻¹) at the inlet and outlet of the reactor, respectively.

Detection of other products (i.e., C₂H₆, C₂H₄, CH₃OH, and C₂H₅O), as well as deposited carbon, was in negligible amounts; thus, only CO₂, CH₄, and CO were included in the calculations of the carbon balance in eq 7, which closes within ±10%. The GC injection was performed at least twice for each condition in order to ensure its reproducibility.

\[
\text{carbon balance} (%) = \frac{[CO_2]_{out} + [CH_4]_{out} + [CO]_{out}}{[CO_2]_{in}} \times 100
\]  

Reaction rates were defined in terms of the rate of moles of CO₂ consumed per both mass (rₚ, mol CO₂·g⁻¹·s⁻¹) and surface area (rₙ, mol CO₂·m⁻²·s⁻¹) of the catalyst by eqs 8 and 9, respectively.

\[
r_m = \frac{[CO_2]_{in} \times F_{in} \times X_{CO_2}}{100 \times 60 \times m_{cat} \times V_m}
\]  

\[
r_n = \frac{r_m}{S_{BET}}
\]  

where [CO₂]_{in} (%) v/v is the inlet CO₂ concentration. F_{in} (mL·min⁻¹) is the total flow rate at the inlet of the reactor. X_{CO₂} (%) is the CO₂ conversion at 300 °C. m_{cat} (g) is the mass of the catalyst. S_{BET} (m²·g⁻¹) is the BET specific surface area of the catalyst. V_m is the gas molar volume at 25 °C and 1 bar (24,436 cm³·mol⁻¹). The k rate constant (m³/s·kg) was calculated using eq 10, while the activation energy (E_a) was derived from an Arrhenius plot.
\[ k = \frac{-F_{in} \times \ln(1 - X_{CO_2})}{60 \times 100 \times m_{cat}} \]  

(10)

Notes

The authors declare no competing financial interest.

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