Influence of the Calcination Technique of Silica on the Properties and Performance of Ni/SiO₂ Catalysts for Synthesis of Hydrogen via Methane Cracking Reaction

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ABSTRACT: Deactivation of catalysts due to rapid blocking of active surfaces and pores is a major problem for methane cracking. The removal of the template using different calcination methods contributes to the different characteristics of catalyst support. Therefore, silica supports were prepared with the sol–gel method, where sodium silicate and chitosan are a silica source and a template, respectively. Calcination using a microwave muffle furnace (MWF) was preferred over the conventional electric muffle furnace at the heating rates of 2 and 17 °C/min (CEF2 and CEF17, respectively) in order to remove the chitosan template. A nickel nitrate precursor was loaded onto the obtained silica supports by the incipient wetness impregnation method. The properties of the silica support and the Ni/SiO₂ catalysts were characterized by means of N₂-sorption, X-ray diffraction, scanning electron microscopy—energy-dispersive X-ray, field emission transmission electron microscopy, and H₂ temperature-programmed reduction. The catalytic activity was evaluated using a fixed-bed reactor at 550 °C with a CH₄/N₂ ratio of 1:4 in the feed. The amount and the allotropes of carbon deposited on the spent catalysts were investigated using thermogravimetric/differential thermal analysis. The results showed that the SiO₂-MWF support had a higher surface area and a larger pore volume of a mesoporous structure with larger interparticle channels than that of the SiO₂-CEF supports. This leads to the higher dispersion of Ni metal particles over and inside the interparticle channels of the SiO₂-MWF support. This provided a higher metal–support interaction, resulting in lower rates of methane conversion and carbon deposition on the catalyst surface than those of Ni/SiO₂-CEF catalysts. However, it displayed a lower bed pressure. It was found that the carbon fibers deposited on all the catalysts were multiwalled carbon nanotubes (MWCNTs). Additionally, the base-growth mechanism of MWCNTs was only exhibited by the Ni/SiO₂-MWF catalyst.

1. INTRODUCTION

Methane, classified as one of the greenhouse gases, is the main reason behind global warming, which is emitted into the atmosphere through industrial processes and human activities. The utilization of methane as a feedstock for producing value-added chemicals is hence the most promising way to reduce its emission. Methane cracking is an interesting reaction in the viewpoint of hydrogen production nowadays. Moreover, even carbon coproducts of this reaction can be potentially used in industrial applications as composite materials, catalysts, adsorbents, electrodes, and so forth. However, these may play a role in the deactivation of catalysts, as they rapidly block the active surface of metal catalysts. Coking is a major concern regarding the catalyst deactivation for methane cracking reaction. It results from the decomposition of adsorbed methane into carbon and hydrogen over metal catalyst, covering the metal-active size and blocking the pore of the catalyst. It leads to the loss of catalytic activities.

Several investigations on methane cracking over transition-metal catalysts, such as Ni, Fe, Co, Pd, Mo, and so forth, have been reported in many literature studies since the early 60s. It has been found that Ni-based catalysts showed significantly higher catalytic activity and lower cost, which are favorable for this reaction. Garcia-Vargas et al. reported that Ni particle...
size and dispersion are key factors that affect the carbon deposition mechanism. Highly dispersed tiny particles avoid carbon deposition, which could cause irreversible catalyst deactivation and/or the increase of catalytic bed pressure. Several researchers studied the effect of Ni catalyst synthesis condition on Ni particle size and dispersion and related it to methane cracking productivity and the life of a catalyst.10,11 In addition, many publications have shown that the physicochemical properties of catalytic supports could play an important role in influencing the catalytic performance and deactivation of catalysts.1,7,9,10 For example, the effect of support materials for Ni-based catalyst on the performance of methane cracking reaction has been examined by Takenaka et al.10 and reported that silica is one of the most effective supports for producing hydrogen and carbon nanofibers among various supports.9,11 The pore characteristic of silica supports is also crucial in influencing the ability of catalysts, especially in methane cracking reaction with carbon accumulated over the catalyst surface. A template is necessary to create pores on the silica support. Chitosan is often used as a template for synthesis of porous silica because it can easily be removed through calcination and has reasonable commercial cost.12 The template removal condition by calcination affects the pore characteristic of silica support. However, very limited information is available on the impact of calcination for removing the template of silica support on the catalytic performance and life of catalysts, especially in the case of rapid deactivation of catalysts. Recently, microwave irradiation has been effectively used for producing ordered porous materials.13 It provides a rapid and homogeneous heating of the entire sample, enhancing reaction rates, facilitating the formation of uniform nucleation centers, and is energy-efficient and environmentally friendly.14

This study, therefore, aims to investigate the influence of the process of calcination for the removal of chitosan template on the resulting Ni dispersion and characteristics of Ni/SiO2 catalysts as well as their activity in catalyzing the methane cracking reaction. In this work, silica support was prepared by sol–gel method using sodium silicate as a silica source and chitosan as a template. In order to remove the chitosan template, a microwave furnace was used as a calcination technique compared to the conventional electric furnace with different heating rates. It is hypothesized that different calcination conditions for template removal of the SiO2 support affects the life and catalyst performance of the SiO2-supported Ni catalyst.

2. RESULTS AND DISCUSSION

2.1. Textural Properties and Elemental Analysis. The textural properties of silica support and Ni/SiO2 catalysts, namely, specific surface area, pore diameter, and pore volume, were studied with N2 isothermal adsorption–desorption (Table 1). Chitosan template removal using a microwave muffle furnace (MWF) not only produces higher surface area silica support but also produces larger total pore volume compared to those of silica supports obtained from the template removal using electric muffle furnace, because chitosan has high dielectric constant and dielectric loss (80 and 120 at 25 °C, respectively),15 which makes it transparent to microwave. The absorbed energy is then converted into heat, causing rapid temperature increase and hence the accelerated decomposition of chitosan within the silica support.16 Therefore, the shrinkage of the silica support in the case of calcination using a MWF was lower than that in the cases of calcinations using a conventional electric muffle furnace. Tian et al.17 suggested that the usage of microwaves in order to remove the template of siliceous porous materials had many advantages, namely, it provides very fast and complete removal of the template while providing very low structure shrinkage. It has been found that the specific surface area and pore volumes of all supports are drastically decreased after the loading of nickel metal precursor. These results indicated that the pore of the silica support samples was partially blocked by NiO particles. The N2-sorption results shown in Figure 1a reveal that the isotherms of all silica products exhibited the composite isotherm between types IV and II with categorized H3 hysteresis loops at high relative pressure, indicating the existence of mesoporous structures. The results implied that the usage of either a microwave or a conventional electric muffle furnace to remove chitosan template could produce mesoporous silica supports, which attributed to the slit-type pores associated with interparticle porosity generated in solids with platelike morphology.15,18 Figure 1b shows pore size distribution for all removed chitosan template supports. It is apparent that SiO2-MWF exhibits more uniform pore size of mesoporous than SiO2-CEF2 and SiO2-CEF17 supports. The N2-sorption isotherm and pore size distribution of loaded Ni on all supports are shown in Figure 2a,b, respectively, revealing the same characteristics for all supports with lower volumes of N2-sorption compared to unloading support (Figure 1), which causes their pore volume to reduce because of partial blocking by NiO particles.

The influences of calcination technique on the morphologies and porous structures of the NiO/SiO2 catalysts were characterized by scanning electron microscopy (SEM). Figure 3 shows the SEM image of NiO/SiO2-CEF2, NiO/SiO2-CEF17, and NiO/SiO2-MWF samples. It is clearly observed that the SiO2-MWF support exhibited a highly porous and spongelike structure with large pore size and interparticle channels. On the other hand, the SiO2-CEF2 and SiO2-CEF17 support exhibited dense aggregates of smaller-sized particles and interparticle channels. The mesopores of silica support were formed as the result of primary silica nanoparticle aggregation produced by hydrolysis–condensation of sodium silicate,19 while the formation of the interparticle channels between mesoporous silica particles was caused by template removal during the calcination process.20 Calculation permits

| Table 1. Textural Properties of Silica Support and Catalyst |
|---------------------------------|
| Sample                          | Surface area (m²/g) | Pore diameter (nm) | Pore volume (cm³/g) | Crystallite diameter (nm) |
|---------------------------------|
| Unloaded Porous Silica Supports | 432                | 9.49               | 0.59                | 13.30                |
| Load Porous Silica Supports     | 358                | 9.38               | 0.50                | 16.07                |
| Ni/SiO2-CEF2                    | 370                | 9.41               | 0.51                | 17.72                |
| Ni/SiO2-CEF17                   | 377                | 9.49               | 0.54                | 15.98                |

aSpecific surface area calculated by BET method. bPore diameter measured by BJH desorption method. cAverage diameter of NiO and Ni crystallite determined by XRD (Scherrer’s equation).
the removal of organic compounds presented in the structure of chitosan, which can be involved in the formation of both hydrogen and intermolecular bonding with silica. When calcination takes place at 600 °C for those compounds decomposed, the intermolecular force and hydrogen bonding were eliminated, resulting in the enlargement of voids in the chitosan network.\textsuperscript{21,22} With the use of microwave calcination furnace, the largest interparticle channels of silica are generated as compared to the electric furnace. This is due to the higher calcination rate obtained from the microwave furnace. Still, SiO\textsubscript{2}-CEF\textsubscript{17} was provided by the removal of the chitosan template by applying an equivalent heating rate to the microwave furnace (17 °C/min), but smaller channels and more dense structures were obtained. These results are obtained because of the occurrence of shrinkage.\textsuperscript{23} In addition, the textural properties were successfully improved by microwave technique as reflected by the large surface areas, high total pore volume, and large primary pore sizes. These results corresponded to N\textsubscript{2} sorption results (Table 1). Therefore, it is concluded that microwave calcination can contribute to the performance of the porous structure with high surface area.

The crystallographic structures and types of metal oxide species of the calcined catalysts were analyzed by X-ray diffraction (XRD). As shown in Figure 4a, the strong broad peaks in the range of 2\(\theta\) = 15–25° can be assigned to amorphous silica.\textsuperscript{24} It is clearly observed that all catalysts show similar diffraction peaks at 2\(\theta\) of 37.35, 43.35, 63, and 75.5 corresponding to the (111), (200), (220), and (311) planes for a typical cubic phase of NiO.\textsuperscript{1,2} The NiO crystallite sizes estimated from the full width at half-maximum of the (200) plane according to Scherrer’s equation are listed in Table 1. It is noticeable that the average particle sizes of NiO deposited over all SiO\textsubscript{2} supports are larger than their silica pore diameter. It is indicated that most of the NiO particles were deposited on

![Figure 1.](image1.png) (a) N\textsubscript{2}-adsorption–desorption isotherms and (b) pore size distribution of removed chitosan template silica supports.

![Figure 2.](image2.png) (a) N\textsubscript{2}-adsorption–desorption isotherms and (b) pore size distribution of Ni-loaded porous silica supports.

![Figure 3.](image3.png) SEM-EDX images of (a,b) NiO/SiO\textsubscript{2}-CEF\textsubscript{2}, (c,d) NiO/SiO\textsubscript{2}-CEF\textsubscript{17}, and (e,f) NiO/SiO\textsubscript{2}-MWF catalysts.
the external surface of their silica supports.\textsuperscript{25} However, the NiO crystallite size over SiO\textsubscript{2}-MWF support showed the smallest size among the NiO over SiO\textsubscript{2}-CEF2 and SiO\textsubscript{2}-CEF17 supports. Therefore, the NiO particles had a greater opportunity to be positioned in the pores and interparticle channels of the supports in the case of SiO\textsubscript{2}-MWF supports compared to those over other SiO\textsubscript{2} supports.

Figure 4b depicts the wide-angle XRD patterns of the Ni catalysts obtained by the reduction of NiO under hydrogen atmosphere at 700 °C, which found that all catalysts exhibited similar diffraction peaks at 2\(\theta\) = 44.5, 51.8, and 76.4, corresponding to (111), (200), and (220) planes of metallic Ni with the absence of NiO peaks observed.\textsuperscript{26} This suggests that during the reduction of the catalysts, Ni\textsuperscript{2+} of NiO can be completely reduced to the active form of Ni\textsuperscript{0}.\textsuperscript{27} Besides, the Ni crystalline size, as listed in Table 1, can also be calculated by Scherrer’s equation from the (111) plane. As can be clearly seen, SiO\textsubscript{2}-MWF is the smallest crystallite size of 13.30 nm. On the other hand, SiO\textsubscript{2}-CEF17 is the largest crystallite size of 14.50 nm, which may be due to the aggregation of Ni particles during the reduction process.\textsuperscript{28}

The metal to support the interaction of catalyst plays an important role in controlling the accessibility of active species to reactant and the agglomeration tendency of active metals that have a substantial influence on catalytic performance.\textsuperscript{29} The reducibility of NiO over SiO\textsubscript{2}-CEF2, SiO\textsubscript{2}-CEF17, and SiO\textsubscript{2}-MWF is determined by the H\textsubscript{2} temperature-programmed reduction (TPR) profiles, as shown in Figure 5. It can be observed that a similar reduction process occurred. The appearance of reduction peaks for NiO/SiO\textsubscript{2}-CEF2 at 330 and 430 °C and NiO/SiO\textsubscript{2}-CEF17 and NiO/SiO\textsubscript{2}-MWF at 420 and 450 °C, respectively, are assigned to the reduction of bulk NiO in the outermost surface, having less interaction with the supports. In contrast, the peak at higher temperatures of 550, 550, and 630 °C is assigned to the reduction of NiO in the subsurface, having strong interaction with the SiO\textsubscript{2} supports. It is confirmed that NiO over all SiO\textsubscript{2} supports was completely reduced at temperatures not exceeding 700 °C, consistent with the XRD results of Ni/SiO\textsubscript{2} in the absence of NiO pattern. In addition, it could be clearly observed that NiO over SiO\textsubscript{2}-MWF was reduced at the highest reduction temperature.\textsuperscript{25} Considering the isolation effect reported by Hu\textsuperscript{30} there are two possible types of NiO species in the NiO/SiO\textsubscript{2} catalysts: (1) NiO surrounded by SiO\textsubscript{2} and (2) NiO surrounded by NiO. The first type of NiO has lower reducibility than the second type of NiO because the first type of NiO was isolated by SiO\textsubscript{2}, hindering the formation of a Ni–Ni bond while removing the O atom by hydrogen. Therefore, the results indicate that microwave calcination enhanced the incorporation between the NiO and SiO\textsubscript{2} in the NiO/SiO\textsubscript{2} catalyst, resulting in more NiO surrounded by SiO\textsubscript{2} and requiring a higher H\textsubscript{2} reduction temperature.\textsuperscript{31}

Field emission transmission electron microscopy (FE-TEM) images of the reduced Ni/SiO\textsubscript{2} catalysts (Figure 6) also show Ni particle sizes ranging from ca. 5.88 to 47.06 nm for Ni/SiO\textsubscript{2}-MWF, which are smaller than Ni particles over SiO\textsubscript{2}-CEF2 and SiO\textsubscript{2}-CEF17, supporting the XRD results. The metal dispersion of Ni over each SiO\textsubscript{2} support was roughly observed using energy-dispersive X-ray (EDX), as shown in Figure 3b,d,f. Still, these catalysts have similar actual amount of nickel, approximately 10% wt as listed in Table 2. The lowest amount of Ni particles dispersed on the SiO\textsubscript{2}-MWF support. This might be due to its large pore diameter and
interparticle channels; smaller-sized Ni particles could easily penetrate into the pores and deposit in higher amounts. This is consistent with the N2-sorption results (Table 1), which can observe the highest decreasing pore volume of SiO2-MWF support after Ni loading from 0.7 to 0.54 cm3/g (accounted for 22.86%). In addition, the highest Ni dispersion and the smallest Ni particle size are observed only on the SiO2-MWF support compared with the SiO2-CEF2 and SiO2-CEF17 supports. The dispersion of Ni metal over SiO2 support could also be confirmed by the FE-TEM image, as shown in Figure 6. It exhibited high Ni metal dispersion in the case of Ni/SiO2-MWF catalyst. This confirmed that the SiO2-MWF support might contribute to the dispersion of Ni metals both on the surface and in the pores/interparticle channels of support.

2.2. External and Internal Diffusion Elimination. To investigate the influence of calcination process on the activity and stability of Ni/SiO2 catalysts in methane cracking reaction by neglecting the effect of mass transfer, the external and internal diffusion elimination was considered. The elimination of external diffusion was conducted by changing the space velocity of the reactant gases. The space velocity was varied by changing the total flow rate of the reactant gases, while maintaining a constant weight of the catalyst. The total flow rate of the reactant gases was varied by 80, 100, and 120 mL/min and 0.1 g of catalysts with 53−106 μm were employed. Therefore, the investigated gas hourly space velocities (GHSVs) were 48 000, 60 000, and 72 000 mL/g·h, respectively. The elimination of internal diffusion was practiced by changing the particle size of catalysts, while maintaining a constant GHSV of the reactant gases. The particle size of Ni/SiO2-CEF17 catalyst was varied by <53, 53−106, and 106−149 μm. The GHSV of the reactant gases was maintained at 60 000 mL/g·h. Therefore, 0.1 g of catalysts and the total flow rate of the reactant gases of 100 mL/min were employed. The reaction was carried out at a temperature of 550 °C under atmospheric pressure for 60 min of reaction time. Figures S1 and S2 show that the GHSV in the range of 48 000−72 000 mL/g·h and the particle size of catalysts in the range of <53−149 μm have no obvious effects on methane conversion and hydrogen yield in methane cracking reaction. It confirmed that the use of 60 000 mL/g·h GHSV of reactant gases and catalysts with 53−106 μm particle size, used in this study to monitor the performance of Ni/SiO2 catalysts in methane cracking reaction, could eliminate the effect of external and internal diffusions.

2.3. Performance Evaluation of Ni/SiO2 Catalyst in Methane Cracking Reaction. The activities of the prepared Ni/SiO2 catalysts for methane cracking reaction were investigated by testing in a catalytic fixed-bed reactor at 550 °C throughout 360 min of time on stream. On the basis of the lower limits of gas chromatography analysis (ppm), only hydrogen was obtained as a gaseous product over all catalysts, without other hydrocarbon products being detected. Figure 7a shows that the methane conversions of Ni/SiO2-CEF2 and Ni/SiO2-CEF17 catalysts were higher than that of Ni/SiO2-MWF catalyst in the initial period of reaction, indicating that they are more favorable in the methane cracking reaction than Ni/SiO2-MWF catalyst in the first period of reaction. This result was due to most Ni particles dispersed on the surface of SiO2-

Table 2. Amount of Carbon Product of Ni/SiO2 Catalysts in Methane Cracking Reaction

| catalyst       | total amount of carbon% | amount of nickel% w/w | relative carbon yield per reaction time%/min |
|----------------|-------------------------|-----------------------|--------------------------------------------|
| Ni/SiO2-CEF2   | 67.92                   | 10.97                 | 5.16                                       |
| Ni/SiO2-CEF17  | 62.84                   | 10.39                 | 9.30                                       |
| Ni/SiO2-MWF    | 71.77                   | 10.80                 | 1.85                                       |

Calculated from TG analysis data. Determined by ICP−OES. Calculated as the relative carbon yield per reaction time (%/min) = (weight of deposited carbon on the catalyst × 100)/(weight of metal content in the catalyst × reaction time).
CEF2 and SiO2-CEF17 support, as presented in the EDX results (Figure 3). It indicated more active sites, which can easily react with methane, leading to a faster reaction rate in an initial period of reaction. However, the methane cracking reactions over Ni/SiO2-CEF2 and Ni/SiO2-CEF17 catalysts were unable to continue until 360 min of time on stream because a serious pressure drop followed by plugging of the reactor was observed. There was high pressure inside the packed bed tube reactor, gradually increasing to a severe pressure drop of 10 bars, as depicted in Figure 7c. This was caused by the formation of carbon fibers deposited over the catalysts’ surface. A TG analysis confirmed that the increase in pressure drop was caused by the carbon deposition on the catalyst bed.7,32 This is discussed further in Section 2.4. Therefore, for safety reasons, catalyst activity testing was stopped when the pressure drop reached 10 bars, even though they had not completely deactivated. In contrast, Ni/SiO2-MWF catalyst contains a smaller amount of Ni-active sites over its surface, owing to the deposition of Ni particles inside the SiO2-MWF support, as discussed above. This leads to lower methane conversion than Ni/SiO2-CEF2 and Ni/SiO2-CEF17 catalysts. It is clearly noticeable that the methane cracking reaction over Ni/SiO2-MWF could be carried out with a gradual decrease of methane conversion and hydrogen yield until the end of time for testing throughout 360 min.

Considering the hydrogen yields of all catalysts shown in Figure 7b, it has been found that they are in the same trend as gradually decreasing. It is remarkable to notice that Ni/SiO2-CEF catalysts have higher methane conversion; on the other hand, Ni/SiO2-CEF2 catalyst has the same hydrogen yield while Ni/SiO2-CEF17 catalyst has lower hydrogen yield compared to Ni/SiO2-MWF catalyst. It is due to the fact that Ni/SiO2-CEF catalysts have higher reactivity that generates more carbon fibers. Thus, hydrogen product might be adsorbed inside carbon fibers. The effect of the carbon product formed on the spent Ni/SiO2-CEF17 and Ni/SiO2-MWF catalysts, on the H2 adsorption performance at 550 °C of reaction temperature, was investigated. It has been found that the carbon formed on the spent Ni/SiO2-CEF17 catalyst can adsorb higher amounts of H2 gas (∼12.09% of H2 adsorption) as compared to the carbon formed on the spent Ni/SiO2-MWF catalyst (∼10.32% of H2 adsorption). This result could be explained by the H2 product being adsorbed on carbon products (carbon fibers or carbon nanotubes), resulting in lower hydrogen detection, which was in agreement with the results reported by Kahle et al.33

2.4. Post-Reaction Study of the Spent Ni/SiO2 Catalysts. All spent catalysts were investigated in order to determine the amount and allotropes of carbon products. The simultaneous TG/differential thermal analysis (TG/DTA) technique was applied and the results are shown in Figure 8.

Figure 7. (a) Methane conversion and (b) hydrogen yield in methane cracking reaction over Ni/SiO2 catalysts and (c) profile of pressure occurs in packed bed reactor during catalytic testing.

Figure 8. TG/DTA curve of spent (a) Ni/SiO2-CEF2, (b) Ni/SiO2-CEF17, and (c) Ni/SiO2-MWF catalyst after being used in methane cracking reaction.
The oxidation of raw MWCNTs started at 420 °C under air atmosphere with no phase change or any oxidation reaction noted during the reaction. This result indicates that Ni/SiO2-CEF2 and Ni/SiO2-CEF17 catalysts can convert more methane into MWCNTs in a comparative period. In addition, the metal—support interactions were also found to play a crucial role in the growth mechanism. The strong metal—support interaction yielded a base-growth mechanism, whereas the weak metal—support interaction leads to the formation of a tip-growth mechanism. This is consistent with the results of this work, which found that the smallest NiO size had the strongest interaction with SiO2-MWF support and generated base-growth MWCNTs, as shown in Figure 9c. On the other hand, Ni/SiO2-CEF2 and Ni/SiO2-CEF17, which are larger amounts of larger Ni particle sizes dispersed on the support surface and weaker interaction between the metal and support, generated tip-growth MWCNTs. This evidence is consistent with the activity results confirming that Ni/SiO2-MWF has a lower methane conversion than Ni/SiO2-CEF2 and Ni/SiO2-CEF17 catalysts in the initial period because Ni particles are more deposited inside the pore and interparticle channels. Ni particles, located inside the pores, had strong interactions with the SiO2 support. This led to carbon covering on Ni particles and the carbon nanofibers to grow through base-growth mechanism. Additionally, it was difficult to grow CNTs inside the hollow of a pore because the blockage of Ni particles by graphite prevents them from growing outward.

It is clearly seen that the derivative weight loss peaks for the carbon deposited on each catalyst appeared at a temperature range of 562–706.1, 602.1–710.8, and 553.3–670 °C for Ni/SiO2-MWF, Ni/SiO2-CEF2, and Ni/SiO2-CEF17 catalysts, respectively. It was observed that all catalysts were oxidized at high temperature (above 550 °C), indicating the presence of multiwalled carbon nanotubes (MWCNTs) on all of the catalysts. This conclusion is obtained because of the fact that MWCNTs are thermally stable up to 420 °C under air atmosphere with no phase change or any oxidation reaction taking place. The oxidation of raw MWCNTs started at 420 °C and finished at 630 °C, while the oxidation of graphitized MWCNTs took place between 640 and 780 °C. It can be observed that highly graphitized MWCNTs occurred over Ni/SiO2-CEF2 and Ni/SiO2-MWF catalysts.

The efficiency of catalysts to grow carbon nanotubes can be reflected by the weight loss of the carbon deposits. The amount of MWCNTs performed over Ni/SiO2-CEF2, Ni/SiO2-CEF17, and Ni/SiO2-MWF catalysts (Table 2) yielded 67.92, 62.84, and 71.77%, respectively. It was found that Ni/SiO2-MWF yielded the highest amount of MWCNTs among both Ni/SiO2-CEF catalysts because it is the longest usable catalyst. However, Ni/SiO2-CEF2 and Ni/SiO2-CEF17 catalysts are used in shorter periods of 120 and 80 min of time on stream, respectively, but MWCNT amounts formed on these catalysts are almost equal to that on Ni/SiO2-MWF catalyst used in a period of 360 min. This result indicates that Ni/SiO2-CEF2 and Ni/SiO2-CEF17 catalysts can convert more methane into MWCNTs in a comparative period. In addition, the rate of carbon formation can be considered as the relative carbon yield per reaction time listed in Table 2. It was found that the fastest carbon deposition rate of Ni/SiO2-CEF17 catalyst was observed. It showed that higher Ni aggregated over catalyst surface can accelerate the rate of carbon deposition on the catalysts. This was consistent with the results of reactivity results, Ni/SiO2-CEF17 showed fastest rate of methane conversion yielding fastest rate of carbon deposition.

Gohier et al. discussed that particle size was not the only condition which controls the growth mechanism of carbon nanotubes but is one of the conditions for choosing tip or base growth. In addition, the metal—support interactions were also found to play a crucial role in the growth mechanism. The strong metal—support interaction yielded a base-growth mechanism, whereas the weak metal—support interaction leads to the formation of a tip-growth mechanism. This is consistent with the results of this work, which found that the smallest NiO size had the strongest interaction with SiO2-MWF support and generated base-growth MWCNTs, as shown in Figure 9c. On the other hand, Ni/SiO2-CEF2 and Ni/SiO2-CEF17, which are larger amounts of larger Ni particle sizes dispersed on the support surface and weaker interaction between the metal and support, generated tip-growth MWCNTs. This evidence is consistent with the activity results confirming that Ni/SiO2-MWF has a lower methane conversion than Ni/SiO2-CEF2 and Ni/SiO2-CEF17 catalysts in the initial period because Ni particles are more deposited inside the pore and interparticle channels. Ni particles, located inside the pores, had strong interactions with the SiO2 support. This led to carbon covering on Ni particles and the carbon nanofibers to grow through base-growth mechanism. Additionally, it was difficult to grow CNTs inside the hollow of a pore because the blockage of Ni particles by graphite prevents them from growing outward.

Therefore, the strong interaction between Ni and support, related to mainly base-growth MWCNT generation, can be observed in the case of Ni/SiO2-MWF, and the good dispersion of Ni over the support with low shrinkage of silica support can prolong the life of Ni/SiO2 to longer than 360 min. In addition, the Ni/SiO2-MWF provided the longer life more than 40% with higher hydrogen yield compared to Ni/SiO2 catalysts for methane cracking reaction reported by Tanggarnjanavalukul et al. and Donphai et al.

The SEM image of MWCNTs deposited over Ni/SiO2-CEF2, Ni/SiO2-CEF17, and Ni/SiO2-MWF catalysts is shown in Figure 10. It is clearly observed that highest dense MWCNT fibers were generated over Ni/SiO2-CEF17 catalyst, followed by Ni/SiO2-CEF2 and Ni/SiO2-MWF catalyst, respectively. This result may be obtained because the Ni/SiO2-MWF catalyst had a large cavity obtained from the interparticle
channels. In addition, the largest average size of MWCNTs over Ni/SiO2-MWF catalyst was obtained as a result of the longest usable catalyst.

The performances of the catalysts in this work were compared to those of previously reported ones, as listed in Table 3. The study of the relative high nickel loading and the effect of promoter addition produced higher methane conversion and hydrogen yield as reported by Zhang and Amiridis, Zhu et al., Bayat et al., and Pudukudy et al. This indicates that the relative high nickel loadings and operating temperature are favorable for the methane cracking process. In the case of low nickel loading (ca. 10% Ni) without any promoters and mild operating condition reported in this work and previously by Tanggarnjanavalukul et al. and Donphai et al., it was found that the effect of catalyst support could facilitate the dispersion of nickel, also facilitating high catalytic activity.

The influence of calcination technique on the SiO2 support characteristics is focused. This directly affects Ni/SiO2 catalysts activity in methane cracking and the formation of carbon nanofibers. Obviously, the calcination by MWF generates larger interparticle channels of SiO2 support with higher pore volume of mesoporous structure with larger interparticle channels, significantly facilitating the dispersion of Ni particles on the support surface of Ni/SiO2-MWF catalyst. In contrast, Ni/SiO2-CEF2 and Ni/SiO2-CEF17 showed higher catalytic reactivity for the methane cracking reaction in an initial period, even though their high activity leads to the problem of excess bed pressure in the reactor during usage. It can be concluded that different techniques of calcination for template removal significantly affect different textural properties and catalyst characteristics as well as reactivity in the methane cracking reaction, resulting in the different characteristics of carbon nanotubes formed over the spent catalysts.

### 3. CONCLUSIONS

The removal of chitosan template of silica support by calcination using a MWF directly affected the textural properties, reducibility, and catalytic performance in the methane cracking reactions of Ni/SiO2 catalyst. It was found that chitosan template removal by using a MWF (SiO2-MWF) was not only the technique providing the fastest template decomposition but also yielded high surface area and larger pore volume of mesoporous structure with larger intraparticle channels, significantly facilitating the dispersion of Ni particles on the support surface of Ni/SiO2-MWF catalyst. In contrast, Ni/SiO2-CEF2 and Ni/SiO2-CEF17 showed higher catalytic reactivity for the methane cracking reaction in an initial period, even though their high activity leads to the problem of excess bed pressure in the reactor during usage. It can be concluded that different techniques of calcination for template removal significantly affect different textural properties and catalyst characteristics as well as reactivity in the methane cracking reaction, resulting in the different characteristics of carbon nanotubes formed over the spent catalysts.

### 4. EXPERIMENT

#### 4.1. Chemicals.

Chitosan with 90% deacetylation was purchased from Eland Corporation (Nonthaburi, Thailand). Sodium silicate (Na2SiO3: 30 wt % SiO2, 4 wt % NaOH) was obtained from Thai Silicate Chemicals (Bangkok, Thailand). Perfume hydrochloric acid (37%) and glacial acetic acid were purchased from Merck (Darmstadt, Germany). Nickel(II) nitrate hexahydrate was purchased from Sigma-Aldrich (St. Louis, MO). All chemicals and reagents were of analytical grade and used without any further purification.

#### 4.2. Silica Support Preparation.

Silica supports were prepared using the sol–gel method. In the first step, 0.4 g of chitosan was dissolved in 100 mL of 2% (v/v) acetic acid under continuous stirring at 300 rpm for 30 min while temperature was controlled at 40 °C in a water bath. Then, 5.4 g of sodium silicate solution (based on 1.0 g of SiO2) was primarily diluted with 10 mL of deionized water and added to the chitosan solution. The mixture was quickly adjusted to pH 6 by addition of 2.0 M HCl solution. The mixture was left under hydrolysis–condensation reaction for 3 h with continuous stirring and temperature controlled at 40 °C. Next, the resultant mixture was aged in a Teflon-lined autoclave at 100 °C for 24 h. The precipitated products were filtered, washed several times with distilled water, and dried using a microwave oven (LG, MS2343DAR, Seoul, Korea).
Korea) at 600 W for 40 min. Finally, a MWF (CEM, Phoenix, Matthews, NC) and a conventional electric muffle furnace (Nabertherm, HT 16/16, Lilienthal, Germany) were employed to calcine at 550 °C for 4 h with varying heating rates in order to remove chitosan template. Abbreviations for the different techniques were designated as follows:

- MWF denotes calcination using a MWF
- CEF2 denotes calcination using a conventional electric muffle furnace with a heating rate of 2 °C/min
- CEF17 denotes calcination using a conventional electric muffle furnace with a heating rate of 17 °C/min (equivalent to the heating rate of a MWF)

4.3. Loading of Nickel Metal onto Silica Supports. In this study, 10.0 wt % nickel on silica supports was prepared by the incipient wetness impregnation method. Nickel(II) nitrate hexahydrate (0.25 g) [Ni(NO₃)₂·6H₂O] used as nickel precursor was dissolved in 1.3 mL of deionized water and added dropwise into 0.4 g of the prepared silica support. After that, the mixture was dried using a microwave oven (LG, MS2343DAR, Seoul, Korea) at 800 W for 1 min and then calcined using an electric muffle furnace in air at 550 °C for 5 h with a heating rate of 5 °C/min. The catalysts were then ground and sieved to collect the catalyst particles of 53–106 μm (140–270 meshes).

4.4. Catalyst Characterization. The textural properties, namely, specific surface area and pore size distribution of silica supports, both before and after nickel metal loading, were characterized by N₂-sorption using a physisorption analyzer (Quantachrome, Autosorb-1C, Boynton Beach, FL) at −196 °C. Samples were degassed at 200 °C for 4 h prior to measurement. The surface area and total volume were determined according to the standard Brunauer–Emmett–Teller (BET) method and the amount of adsorbed N₂, respectively. The pore diameter distributions were calculated based on desorption isotherms by the Barrett–Joyner–Halenda (BJH) method. The crystallographic structures of catalysts were examined by an X-ray diffractometer (Bruker AXS GmbH, D8 Discover, Karlsruhe, Germany) using Cu Kα radiation at a small angle in the 2θ range of 0–10 and a wide angle in the 2θ range of 10–80, respectively. Average crystallite size was obtained using the global Scherrer’s equation.

The morphology of catalysts was observed by using a scanning electron microscope (FEI, Quanta 450, Hillsboro, OR) equipped with EDX analysis at an accelerating voltage of 10 keV. The samples were coated with a gold layer prior to analysis.

Transmission electron microscopy images were obtained using FE-TEM (JEOL, JEM-3100F, Tokyo, Japan) with an accelerating voltage of 300 kV. Prior to analysis, the samples were dispersed in ethanol and sonicated for 30 min. The suspension was dropped onto a copper grid coated with a carbon film and dried at room temperature.

The actual amounts of nickel in Ni/SiO₂ catalysts were determined by using inductively coupled plasma–optical emission spectrometry (ICP–OES, Optima 8300, PerkinElmer, Singapore). Prior to analysis by ICP–OES, all of the catalyst samples were digested in 10% v/v of HNO₃ by using microwave digestion (Titan MPS, PerkinElmer, Germany).

TPR measurement was performed to identify the reduction temperature and interaction between nickel metal and each support in the temperature range of 50–900 °C using a continuous-flow tube reactor (Inconel-600, o.d. 3/8”) and a heating rate of 5 °C/min. The mixture of H₂ and Ar (9.6% H₂ balanced with Ar) was fed into the catalyst bed and H₂ consumption was monitored using a gas chromatograph (Shimadzu, GC-2014, Kyoto, Japan) equipped with a thermal conductivity detector (TCD). Types of carbon on catalysts were examined by using a simultaneous DTA–TGA analyzer (NETZSCH-Gerätebau GmbH, STA 449F3, Selb, Germany) in air at temperatures ranging from room temperature to 1000 °C.

4.5. Performance of Methane Cracking Reaction. In order to examine the performance of Ni catalysts over different support structures, 0.1 g of each Ni/SiO₂ catalyst was packed in a tube reactor (Inconel-600, o.d. 3/8”). Prior to each experiment being conducted, the catalyst was reduced in H₂ atmosphere (99.99% purity) at a flow rate of 60 mL/min and a temperature of 700 °C (obtained from TPR results) for 2 h. After that, the reactant gases (CH₄ diluted with N₂ at a volume ratio of 1:4) were introduced into the reactor at a total flow rate of 100 mL/min (the GHSV of 60 000 mL/g) and operating temperatures of 550 °C under atmospheric pressure. The obtained gaseous products were analyzed using a Shimadzu gas chromatograph (GC-2014) equipped with a TCD for H₂, CO, and CO₂, while CH₄ analysis was done using a Unibead-C packed column. The percentage of methane conversion and hydrogen yield can be defined as follows:

\[
\text{Methane conversion} (%) = \frac{\text{mole of methane reacted}}{\text{mole of methane input}} \times 100
\]

\[
\text{Hydrogen yield} (%) = \frac{\text{mole of hydrogen produced}}{2 \times \text{mole of methane input}} \times 100
\]

4.6. H₂ Adsorption Experiment. The H₂ chemisorption technique was used in order to prove that the H₂ adsorbed on the carbon formed on the Ni/SiO₂ catalysts, after CH₄ cracking reaction at 550 °C. First, the spent Ni/SiO₂ catalysts were pretreated under Ar flow at 550 °C for 1 h, in order to remove the moisture and clean the surface of the catalyst. Then, H₂ gas was pulse-dosed into the reactor. The amount of H₂ adsorbed was monitored using a gas chromatograph (Shimadzu, GC-2014, Kyoto, Japan) equipped with a TCD.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01904.

Effects of GHSV and catalyst size on methane conversion and hydrogen yield over Ni/SiO₂ catalysts (PDF)

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Notes

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