

การวิเคราะห์คุณลักษณะของโค้กบนตัวเร่งปฏิกิริยา Ni/SiO₂.MgO
จากการรีฟอร์มมิงด้วยคาร์บอนไดออกไซด์ของมีเทนภายใต้การดำเนินงานแบบสับเปลี่ยน



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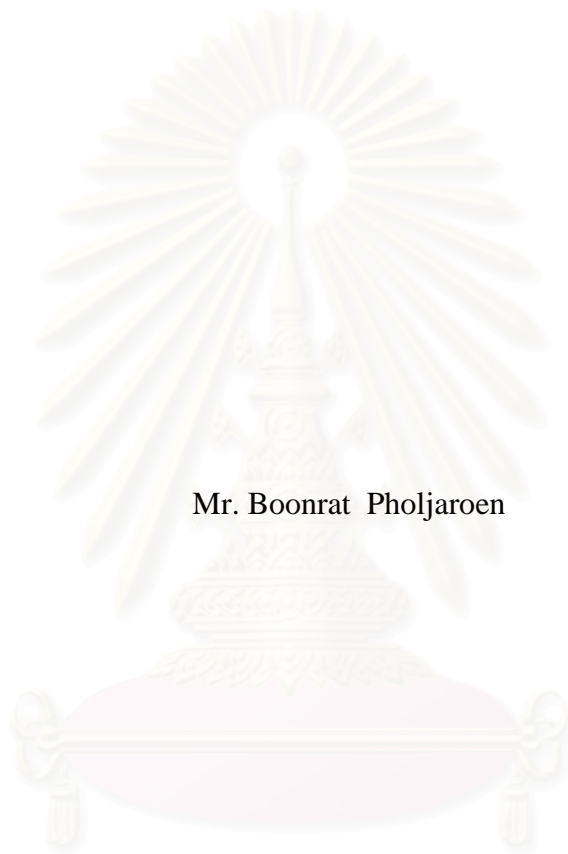
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สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
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ปีการศึกษา 2549

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

CHARACTERIZATION OF DEPOSITED COKE ON
Ni/SiO₂.MgO CATALYST FROM CARBON DIOXIDE REFORMING OF
METHANE UNDER PERIODIC OPERATION



Mr. Boonrat Pholjaroen

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย
A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2006

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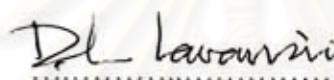
Thesis Title CHARACTERIZATION OF DEPOSITED COKE ON
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REFORMING OF METHANE UNDER PERIODIC
OPERATION

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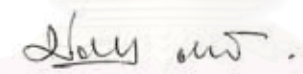
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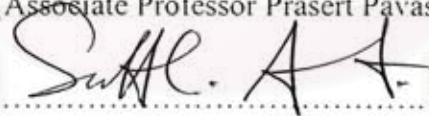
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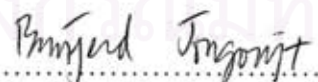

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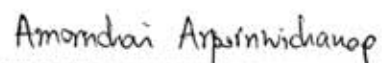
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บุญรัตน์ ผลเจริญ: การวิเคราะห์คุณลักษณะของโค้กบนตัวเร่งปฏิกิริยา Ni/SiO₂.MgO จากการรีฟอร์มมิงด้วยคาร์บอนไดออกไซด์ของมีเทนภายใต้การดำเนินงานแบบสับเปลี่ยน (CHARACTERIZATION OF DEPOSITED COKE ON Ni/SiO₂.MgO CATALYST FROM CARBON DIOXIDE REFORMING OF METHANE UNDER PERIODIC OPERATION) อ. ที่ปรึกษา: รศ.ดร. สุทธิชัย อัสสะบำรุงรัตน์, 69 หน้า.

งานวิจัยนี้ทำการศึกษาการเกิดโค้กที่เกิดในปฏิกิริยาการรีฟอร์มมิงด้วยคาร์บอนไดออกไซด์ของมีเทน ในการดำเนินงานแบบสับเปลี่ยนบนตัวเร่งปฏิกิริยาโลหะนิกเกิลบนตัวรองรับซิลิกอนไดออกไซด์และแมกนีเซียมออกไซด์โดยการใช้วิธีในการวิเคราะห์ต่างๆ ได้แก่ การวัดพื้นที่ผิวของตัวเร่งปฏิกิริยา สแกนนิ่งอิเล็กตรอนไมโครสโคป การกระเจิงรังสีเอ็กซ์และการออกซิเดชันแบบโปรแกรมอุณหภูมิ เพื่อวิเคราะห์คุณลักษณะโค้กที่เกิดขึ้นในช่วงอุณหภูมิปฏิกิริยา 650-750 องศาเซลเซียส ที่เวลาการทำปฏิกิริยาต่างๆ จากการศึกษาพบว่ามีโค้กอย่างน้อยสองชนิดเกิดขึ้นบนพื้นผิวตัวเร่งปฏิกิริยาในช่วงอุณหภูมินี้ ที่อุณหภูมิค่าค่าการเปลี่ยนของมีเทนและคาร์บอนไดออกไซด์และผลได้ของไฮโดรเจนก่อนข้างกลางที่คงที่ตลอดช่วงเวลาทำปฏิกิริยา โค้กปริมาณมากเกิดขึ้นในช่วงเวลาการแตกของมีเทนและบางส่วนถูกเอาออกในช่วงเวลาการรีเจนเนอเรชัน ที่อุณหภูมินี้โค้กส่วนใหญ่จะเกิดในลักษณะเส้นใย ในทางตรงข้ามที่อุณหภูมิสูง ค่าการเปลี่ยนของมีเทนและคาร์บอนไดออกไซด์และผลได้ของไฮโดรเจนลดลงอย่างต่อเนื่องตามเวลาการทำปฏิกิริยาที่เพิ่มขึ้น โค้กที่เกิดขึ้นมีปริมาณน้อยกว่าที่อุณหภูมิค่าแต่เกิดเป็นชนิดห่อหุ้มผิว ดังนั้นจึงกระทบต่อแอกติวิตีของตัวเร่งปฏิกิริยา

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ลายมือชื่ออาจารย์ที่ปรึกษา.....

4870359721 : MAJOR CHEMICAL ENGINEERING

KEYWORDS: CARBON DIOXIDE REFORMING OF METHANE/ PERIODIC OPERATION/ COKE FORMATION/ CATALYST DEACTIVATION/ NICKEL REFORMING CATALYST

BOONRAT PHOLJAROEN: CHARACTERIZATION OF DEPOSITED COKE FORMATION ON Ni/SiO₂.MgO CATALYST FROM CARBON DIOXIDE REFORMING OF METHANE UNDER PERIODIC OPERATION. THESIS ADVISOR: SUTTICHA ASSABUMRUNGRAT, Ph.D., 69 pp.

In this work, the detailed study on the coke formation taking place in the periodic operation of the carbon dioxide reforming of methane on a commercial Ni/SiO₂.MgO catalyst was investigated by using various analytical methods including BET surface area measurement, SEM, XRD, and TPO in order to characterize the coke formed at reaction temperature range of 650-750°C and various reaction times. It was found that at least two different cokes were formed on the surface of catalyst at this temperature range. At low temperature, conversions of methane and carbon dioxide and yield of hydrogen were almost constant throughout reaction time. Coke was formed during the methane cracking period but was incompletely removed in the regeneration period. At this temperature, coke was mostly formed in filamentous form. In contrast, at high temperature, conversions of methane and carbon dioxide and yield of hydrogen decreased continuously with increasing reaction time. A lesser amount of coke was obtained but it was formed in encapsulating form. Thus, it affected the activity of catalyst.

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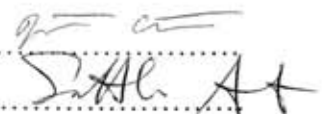
DepartmentChemical Engineering...

Field of Study ..Chemical Engineering.....

Academic year2006.....

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Advisor's signature



ACKNOWLEDGEMENTS

The author would like to express his sincere gratitude and appreciation to his advisor, Associate Professor Suttichai Assabumrungrat, for his invaluable guidance, great encouragement, useful discussions throughout this research and especially, giving him the opportunity to present his research at RSCE conference in Singapore. Special thanks to Professor Shigeo Goto, Professor Tomohiko Tagawa, and Assistant Professor Navadol Laosiripojana for their value suggestion and guidance. In addition, the author would also be grateful to Associate Professor Prasert Pavasant, as the chairman, Assistant Professor Bunjerd Jongsomjit, and Dr. Amornchai Arpornwichanop as the members of the thesis committee. The financial supports of the Thailand Research Fund (TRF), the Graduate School of Chulalongkorn University, and Department of Chemical Engineering are gratefully acknowledged.

Most of all, the author would like to express his highest gratitude to his parents who always take care and encourage him. The most success of graduation is devoted to his parents.

Finally, the author wishes to thank the members of the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University for friendship. To many others, not specifically named, who have provided him with support and encouragement, please be assured that he thinks of you.

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CHAPTER I

INTRODUCTION

1.1 Rationale

Synthesis gas (syngas), a mixture of hydrogen and carbon monoxide, is a potentially important source of many clean fuels and chemicals as well as pollution-free electricity. Synthesis gas can be produced from hydrocarbons by using different methods such as steam reforming, partial oxidation, autothermal reforming and carbon dioxide reforming (or dry reforming) which offer different ratios of hydrogen to carbon monoxide. Carbon dioxide reforming of methane (Eq. 1.1) is an efficient process for producing CO rich synthesis gas. Additionally, this reaction is also considered attractive due to advantages on environmental view point and heat integration.

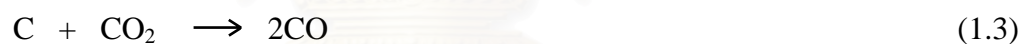


From the carbon dioxide reforming process, synthesis gas produced is in a low H₂/CO ratio which is useful for the synthesis of hydroformylation and carbonylation reactions as well as for methanol, oxygenated compounds and Fischer–Tropsch syntheses.

In an environmental view point, the carbon dioxide reforming reaction helps reduce methane and carbon dioxide which are considered as major greenhouse gases causing the global warming problem. A large amount of carbon dioxide is found in natural gas fields in South-East Asia, and almost remains unused. Methane is a main content in natural gas and can also be produced through anaerobic biomass fermentation of industrial waste water. Thus, the consumption of both gases in this reaction offers a benefit to reduce an environmental problem.

In certain applications, like in proton-exchange membrane (PEM) fuel cell, CO-free hydrogen is necessary for utilization. Although carbon dioxide reforming of methane in steady-state operation can produce hydrogen, the existence of carbon monoxide and carbon dioxide in product stream makes it difficult to separate from hydrogen. A route for solving this problem is the carbon dioxide reforming of methane operated periodically by feeding methane and carbon dioxide alternately.

By thermal catalytic cracking, methane is converted to hydrogen and coke in the first step (Eq. 1.2). Numerous supported transition metal catalysts (Ni, Ru, Rh, Pd, etc.) have been used for this reaction. The noble metal based catalysts are reported to be less sensitive to coking compared to nickel based catalysts but these noble metals are expensive and of limited availability. Nickel catalyst which has low cost is attractive for this reaction. Carbonaceous deposition typically causes plugging and catalytic deactivation problems. Thus, for refreshing the catalyst, catalyst regeneration with carbon dioxide by reverse Boudouard reaction is conducted in the next step (Eq. 1.3). These two steps are repeated alternately.

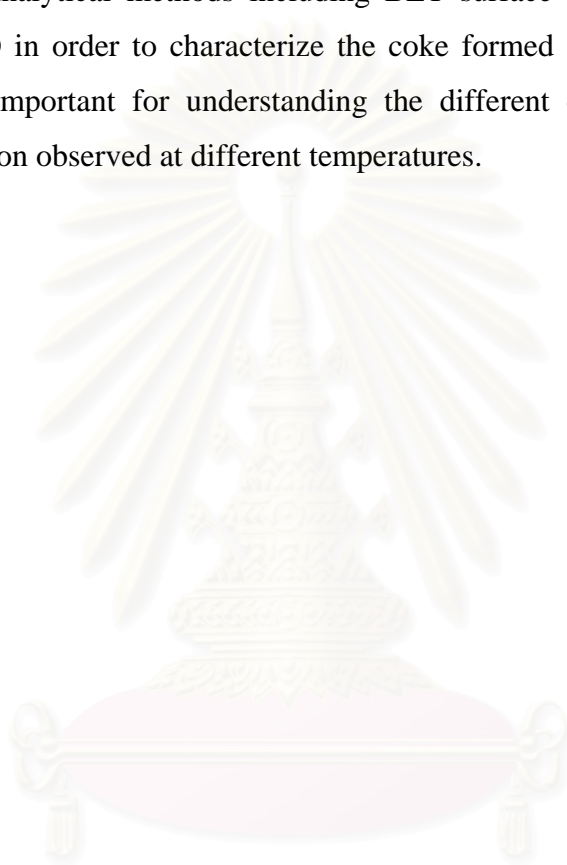


This operation offers a potential benefit on the heat integration within the reactor. The exothermic heat from the catalyst regeneration by reaction of carbon with carbon dioxide to form carbon monoxide can supply the heat for the endothermic methane cracking to generate hydrogen (Monnerat *et al.*, 2001).

In our previous study (Promaros *et al.*, 2007), the performance of the periodic operation for the carbon dioxide reforming of methane over an industrial steam reforming Ni/SiO₂.MgO catalyst compared with the steady-state operation at reaction temperatures 650 and 750°C was investigated. It was found that methane conversions under periodic operation were lower than that of the steady state operation over all ranges of reaction time for both temperatures. In addition, at 650°C the periodic operation provided the comparable hydrogen yield with that of the steady state operation. However, although the yield for the periodic operation was stable over time, similar to that of the steady state operation, the amount of coke deposition was

progressively increased with time unlike that of the steady state operation. It was suggested that different kinds of coke formed could affect performance of the catalyst and the system.

In this work, the detailed study on the carbon formation taking place in the periodic operation of the carbon dioxide reforming of methane was investigated by using various analytical methods including BET surface area measurement, SEM, XRD, and TPO in order to characterize the coke formed at various reaction times. This study is important for understanding the different catalytic behavior of the periodic operation observed at different temperatures.



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CHAPTER II

THEORY

2.1 Carbon Dioxide Reforming of Methane Reaction

In general, the three reactions that attract industrial interest for the conversion of methane to synthesis gas are: the methane steam reforming reaction, methane partial oxidation with oxygen or air, and methane dry reforming with carbon dioxide. The reactions are summarized as shown below:

Methane steam reforming reaction



Methane partial oxidation with oxygen



Methane dry reforming with carbon dioxide



In this study, the reforming of methane with carbon dioxide to synthesis gas is of interest due to a number of advantages over steam reforming or partial oxidation. In a global environmental view point, an advantage of producing synthesis gas by this route is the utilization of methane and carbon dioxide which are well known as green house gases. Moreover, synthesis gas, which is produced from carbon dioxide reforming process with lower H_2/CO ratio, is effective for the synthesis of valuable oxygenated chemicals and for the Fischer-Tropsch synthesis of higher hydrocarbons. Figure 2.1 shows the possible routes for conversion of methane to other valuable products.

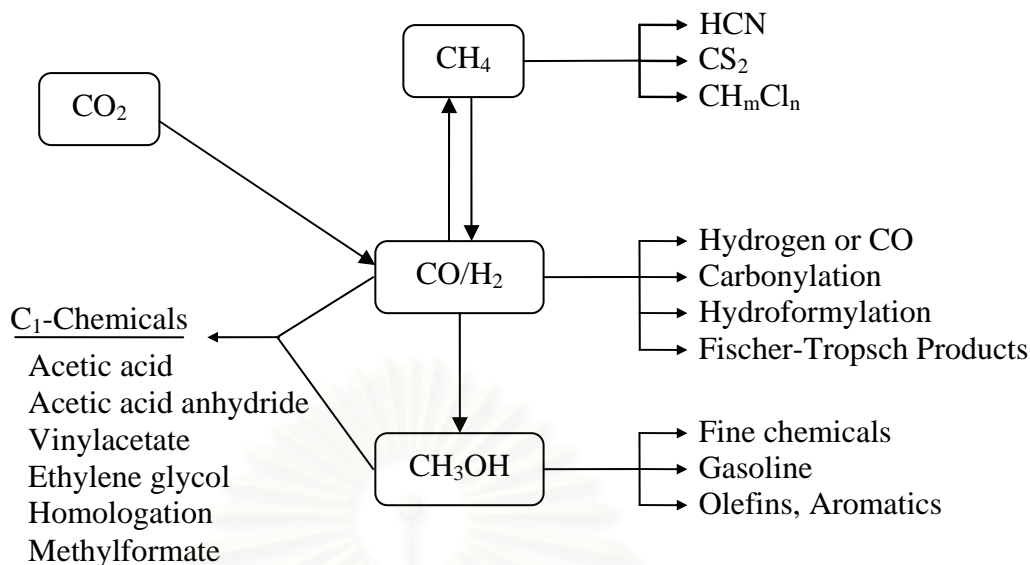


Figure 2.1 Utilization of CH₄ and CO₂ as chemical raw materials

2.1.1 Thermodynamics of carbon dioxide reforming of methane

According to Eq. 2.3, the carbon dioxide reforming of methane is a strongly endothermic reaction, which has similar thermodynamic and equilibrium characteristics to steam reforming reaction (Eq. 2.1). However, the produced synthesis gas has a lower H₂/CO ratio. Due to its endothermic characteristic, reforming is favoured at high temperature. Also, because reforming is accompanied by a volume expansion, it is favoured at low pressure.

Similar to the steam reforming, the carbon dioxide reforming of methane is likely to be conducted under conditions where carbon formation via catalytic cracking of methane (Eq. 2.4) and/or Boudouard reaction (Eq. 2.5) is thermodynamically feasible.



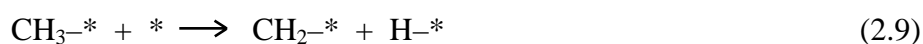
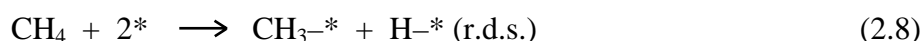
Other reactions which could also have an important influence on the overall product spectrum are:

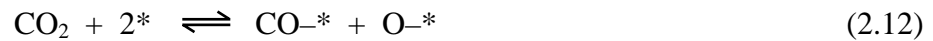


The formation of solid carbon leads to catalyst deactivation and plugging problem in the reactor. Theoretically, the carbon formed should be rapidly consumed by the reverse of reaction (Eq. 2.5), and by the steam/carbon gasification reaction (Eq. 2.6). It should be noted that the formation of water is not desired in this reaction system as it decreases the selectivity of hydrogen.

2.1.2 Reaction mechanism carbon dioxide reforming of methane

Wei and Iglesia (Wei and Iglesia, 2004) investigated the mechanisms for the reactions of CH_4 with CO_2 and H_2O on Rh clusters. Interestingly, they found that reaction rates were proportional to CH_4 partial pressure, but independent of CO_2 and H_2O pressures, which leads to the conclusion of sole kinetic relevance of C–H bond activation steps. Their data indicate that co-reactant (CO_2 or H_2O) activation and its kinetic coupling with CH_4 activation via scavenging of chemisorbed carbon intermediates are fast steps and lead to Rh surfaces essentially uncovered by reactive intermediates. It was also shown that C–H bond activation elementary steps are irreversible and that recombinative desorption steps of H atoms with OH groups to form H_2 or H_2O are quasiequilibrated. The quasi-equilibrated nature of these and other steps confirms that water-gas shift reaction is also at equilibrium. And remarkably, any involvement of the support in the activation of co-reactants was found not to be kinetically relevant. They then arrive at the following mechanism for CH_4 activation ('*' denotes a surface site):





The rate-determining step was found to be the decomposition of methane. The overall CH_4 conversion rates become proportional to CH_4 concentration and independent of the identity or concentration of co-reactants.

2.1.3 Active metal

Usually Ni or the noble metals such as Ru, Rh, Pd, Ir, and Pt are used as the active metal in catalysts. Because of its low costs, Ni is the most widely used metal from this set. Ni, however, is less active (Table 2.1) and usually more prone to deactivation by carbon formation or oxidation.

Table 2.1 Relative activities for steam reforming of methane. $T=550^\circ\text{C}$, $S/C=4$, $P=1$ bar (Rostrup-Nielsen and Hansen, 1993)

Catalyst metal content (wt%)	Relative rate
Ni (16)	1.0
Ru (1.4)	2.1
Rh (1.1)	1.9
Pd (1.2)	0.4
Ir (0.9)	1.1
Pt (0.9)	0.5

The activity of a catalyst is related to the metal surface. This implies that, generally, the catalytic activity benefits from a high dispersion of the metal particles. The structure of the available surface area also strongly influences the catalyst activity. For instance, the close-packed (111) surface of nickel is less active than the more open (110) surface. In fact, metal atoms in surface steps and near defects are much more reactive than metal atoms in the higher coordinated surface terrace sites. For instance, it is known that Ni particles are composed of a number of single crystals (i.e., the metal particles are polycrystalline), which, however, are not completely 'space filling'. Therefore, some lattice distortion is required and these dislocations are expected to play a role in the catalytic reaction.

2.1.4 Catalyst support

The role of the support is to provide a support for the catalytically active metal, in order to obtain a stable and high active surface area. The common supports for methane reforming are α - and γ -Al₂O₃, MgO, MgAl₂O₄, SiO₂, ZrO₂, and TiO₂. These supports have good porosity, which results in a long contact-time between reactants and catalyst. Maintaining a high active surface area is also important. The support can affect the migration and coalescence of metal particles in various ways. Pore structure, morphology, and phase transitions of the support determine the final particle size of the metal.

However, with using the same kind of catalyst support and active component, the difference in catalyst preparation methods would result in different surface morphology of the obtained catalysts. Changing catalyst preparation method can cause different sintering resistant, e.g., from calcinations. It should be noted that for the evaluation of catalyst stability it is essential to consider the effect of sintering under reaction conditions.

The support may also actively participate in the catalytic reaction itself. For instance, supports with a basic nature, such as MgO, are known to enhance the activation of steam (i.e., dissociation into reactive OH and H species). Also,

stabilization of different CH_x -intermediates contributes to the overall reaction mechanism.

2.2 Coke formation

One of the serious problems is the carbonaceous deposition. The formation of coke leads to catalyst deactivation and plugging problem in the reactor. It can be produced by the following reactions:

Catalytic methane decomposition reaction



Boudouard reaction



These cokes have different crystalline structures, morphologies, and reactivities depending on the specific reaction taking place and the reaction conditions. On nickel surfaces, coke formation may take place mainly by three routes.

At lower temperatures (below 500°C), adsorbed hydrocarbons may accumulate on the surface and slowly be transformed into a non-reactive polymer film (gum) blocking and deactivating the surface. This phenomenon can be retarded by hydrogen. Note that because of the endothermic nature of the steam-reforming reaction, high catalyst activity leads to a low temperature at the reaction site, resulting in a higher risk for carbon formation.

At higher temperatures, whisker carbon is the principal product of carbon formation on nickel catalysts. The underlying mechanism is quite comprehensive; it involves diffusion of carbon atoms through the metal particles.

Table 2.2 Routes to coke formation

Carbon type	Reactions involved	Phenomena	Critical parameters
Gum	$C_nH_m \rightarrow (CH_2)_n \rightarrow \text{gum}$	Blocking of surface by polymerisation of adsorbed C_nH_m radicals: progressive deactivation	Low S/C ratio, absence of H_2 , low temperature (below 500°C), presence of aromatics
Whisker carbon, amorphous carbon	$CH_4 \rightarrow C + 2H_2$ $2CO \rightarrow C + CO_2$ $CO + H_2 \rightarrow C + H_2O$ $C_nH_m \rightarrow nC + m/2H_2$	Break-up of catalyst pellet (whisker carbon: no deactivation of the surface)	Low S/C ratio, high temperature (above 450°C), presence of olefins, aromatics
Pyrolytic coke	$C_nH_m \rightarrow \text{olefins} \rightarrow \text{coke}$	Encapsulation of catalyst pellet (deactivation), deposits on tube wall	High temperature (above 600°C), high residence time, presence of olefins, sulfur poisoning

2.3 Periodic operation

Periodic operation is an operation in which one or more inputs into a chemical reactor vary with time, but in such a way that each input is revisited after a time corresponding to the period. The inputs may be varied such as reactor temperature, pressure, flow rate, and flow direction.

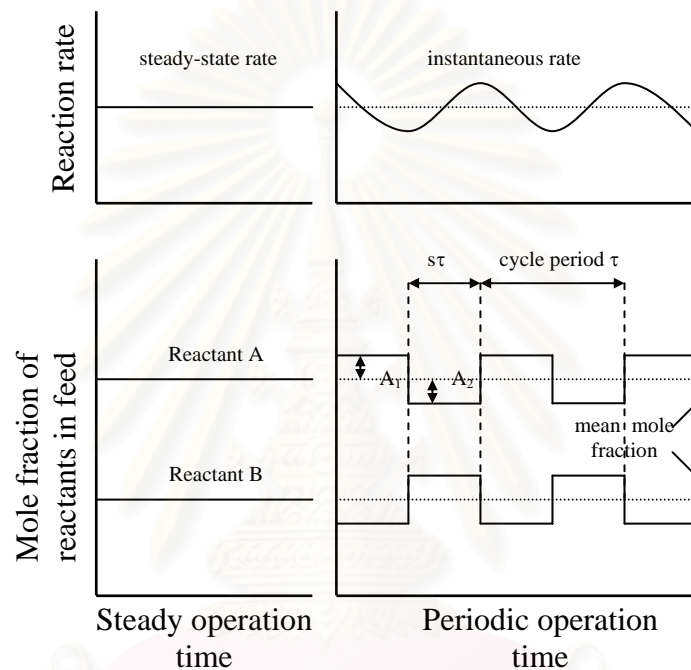


Figure 2.2 Comparison of steady state (left side) and periodic (right side) operation

For understanding about periodic operation shown in Figure 2.2, some cycling variables could be introduced such as:

Cycle period (τ), the time between repetitions of a change in an input condition

Cycle split (s), the duration of one part of cycle relative to the period

Amplitude (A), the change in the value of an input condition from its mean, and mean composition.

The advantages of periodic operation could be summarized as follows:

- Increasing catalyst activity, expressed as conversion or rate of reaction, especially for reactions in which conversion per pass is often limited by equilibrium.
- Periodic operation may be a means of permitting reactors to operate safely in regions of high parametric sensitivity such as operation with exothermic reaction
- Controlling of catalyst deactivation could be attainable.



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CHAPTER III

LITERATURE REVIEWS

3.1 Effects of catalyst and support on carbon dioxide reforming of methane

Takano *et al.* (1994) investigated the carbon dioxide reforming of methane using various Ni catalysts. They reported that the kind of support significantly affects the catalytic activity. Ceramic foam and Al₂O₃ showed higher activities than SiO₂ supports. Alumina-supported catalysts also had stable activities. The addition of MgO to SiO₂-supported catalyst increased catalytic activity but decreased stability. Their later work also found that a rapid pressure drop occurred in the plug flow reactor for nickel catalyst by carbonaceous deposition. Catalysts of larger Ni diameter enhanced plugging of the reactor more readily. A macro-porous ceramic support of high porosity reduced this pressure drop.

Ito *et al.* (1999) proposed a new pretreatment technique, the deposition-removal (D-R) treatment to suppress carbonaceous depositions on Ni/Al₂O₃ catalyst. In the deposition step, deposited carbon whiskers could detach small nickel cores from bulk nickel on the support and growing cores of whisker carbon accelerated the carbonaceous deposition. In the removal step, carbon whiskers were removed by the reaction with carbon dioxide. The D-R treatment caused a part of the nickel to be removed and became inactive species, however, this nickel removed was influenced to reforming activity due to exposure of the new active sites.

Lee *et al.* (2003) found that Ni/Ce–ZrO₂ catalyst displays an excellent performance for the coke on the reactor wall and the surface of catalyst for the tri-reforming of methane. The weak acidic site, basic site and redox ability of Ce–ZrO₂ play an important role in tri-reforming of methane conversion. The modification of Ce-ZrO₂ leads to obtain high and efficient catalytic performances on Ni/Ce–ZrO₂

catalyst compared to commercial catalyst along with stability for production of syngas.

Tsyganok *et al.* (2003) presented the synthesis and structural characterization of new nickel-containing Mg–Al layered double hydroxides (LDH), which adopt a structure in which nickel, chelated with ethylenediaminetetraacetate to a divalent anion $[\text{Ni}(\text{EDTA})]^{2-}$, is nested between brucite-like layers of LDH. The corresponding LDH-derived Ni–Mg–Al mixed oxides demonstrated high and stable catalytic function toward the reaction of methane reforming with carbon dioxide into synthesis gas at 800°C. It is shown that the state of the supported nickel and the coke deposition process were significantly influenced by the method of catalyst preparation.

Roh *et al.* (2004) used a co-precipitation method instead of the conventional impregnation method to prepare nickel oxide dispersed on CeO_2 , ZrO_2 and cubic $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ support to obtain catalysts useful for carbon dioxide reforming of methane reaction. The Ni– CeO_2 and Ni–Ce– ZrO_2 catalysts showed relatively high activity and stability, while the Ni– ZrO_2 catalyst deactivated in the initial stage of the reaction due to serious carbon formation. The co-precipitated Ni–Ce– ZrO_2 catalyst exhibited the highest catalytic activity and the activity was maintained without significant loss during the reaction for 100 h.

Hou *et al.* (2004) reported that Ni/Mg/Al catalysts prepared by coprecipitation method possess the meso-porous structure with higher surface area. The higher surface area of the catalysts allowed the stronger interaction between Ni and Al-Mg, which improved the dispersion of Ni, and retarded the sintering of Ni during the reforming process. The highly dispersed Ni increased the adsorption of CO_2 , exhibiting a higher reforming activity, lower coke formation and a higher stability.

Souza *et al.* (2004) proposed a new activation process for supported nickel catalysts in CO_2 reforming of methane. The activation was performed by heating the catalyst up to 800°C under a mixture of $\text{CH}_4/\text{O}_2 = 2$. During the activation, nickel catalysts are reduced from nickel aluminate species to metallic nickel. The activation with partial oxidation of methane enhanced markedly the activity of these catalysts.

The nickel loading and the support greatly influence the catalyst stability, the conversion increased with Ni loading on alumina support, while the promotion with zirconia did not improve the catalytic behavior. In their previous work (Souza and Schmal, 2003), they proposed that Pt/10%ZrO₂/Al₂O₃ was found to be the most active and stable catalyst for combined CO₂ reforming and partial oxidation of methane.

Juan-Juan *et al.* (2006) investigated the effect of potassium in the catalytic activity and structural properties of a Ni/Al₂O₃ catalyst for the CO₂ reforming of methane. They revealed that potassium promotes the reduction of nickel in the alumina supported catalysts during the activation treatment with H₂ at 773 K. NiK/Al₂O₃ catalysts also hinder the accumulation of coke on the catalyst surface.

3.2 Effects of operating parameters on carbon dioxide reforming of methane

Takano *et al.* (1994) showed the effect of various parameters over Ni/Al₂O₃. The conversion of CH₄ and the yield of H₂ and CO increased with the time factor $W/F_{CH_4,0}$ and reached equilibrium at $W/F_{CH_4,0} = 1.5$ s.kg-cat/mol. Conversion of CH₄ increases with the increase of feed ratio of CO₂/CH₄. A lower CO₂/CH₄ ratio was preferred in order to increase not only the selectivity to H₂ but also carbonaceous deposition. Effect of partial pressure of reactants can be expressed through the simple law equation: $-r_{CH_4} = k(P_{CH_4})^m$ where $m = 0.8-1$. The effect of reaction temperature was also investigated over Ni/SiO₂.MgO catalyst. The pressure drop increased during the reaction period at temperatures below 1000 K did not change at 1030 K, and decreased at 1060 K and 1090 K.

Aiello *et al.* (2000) proposed a potential route to the production of CO-free hydrogen via the direct methane cracking/regeneration cycles. They showed that a 15 wt% Ni/SiO₂ catalyst could be fully regenerated at 923 K with steam for up to 10 successive cracking/regeneration cycles without any significant loss of catalytic activity. XRD analyses indicated no increase in the amount of carbon remaining on the catalyst after successive regenerations and no structural changes in the nickel

particles as the catalyst was cycled between cracking and steam regeneration. SEM micrographs showed that most of the filamentous carbon was removed during steam regeneration, leaving only small pockets of this material which resist this treatment.

Monnerat *et al.* (2001) proposed that the catalytic cracking of methane over nickel gauze was an attractive alternative for the production of CO-free hydrogen. The Ni-grid with Raney-type outer layer was shown to be active for this reaction at relatively low temperatures of 450–500°C. The catalyst deactivated due to intensive coke deposition. Therefore, the reactor was operated periodically with the reaction followed by the catalyst regeneration by burning of coke in oxidative atmosphere. The optimal reaction performance was found to consist of reaction periods of 4 min followed by 4 min regeneration periods.

Diaz *et al.* (2007) studied the influence of some reaction parameters i.e. temperature, chemical nature of pre-treatment gas, mass catalyst on the yield of methane reforming with carbon dioxide on Ni(5%)–Ca(1%)/Activated carbon catalyst synthesized by incipient wetness impregnation at atmospheric pressure. The results show that the best system was pre-treated under He flow at 650°C and then following the reaction at the same temperature. It was also detected that Ca plays a co-support role inhibiting the deactivation of catalyst at long periods of reaction. It can be concluded that it is possible to employ activated carbon as support for methane dry reformation, offering representative methane conversions up to 40% at mild experimental conditions.

3.3 Study on coke formation

Snoeck *et al.* (1997) studied coke formation in thermodynamics and kinetics and proposed possible mechanism of coke formation. The surface reactions, such as the methane cracking or the Boudouard reaction, produce adsorbed carbon atoms. Other types of surface carbon which may encapsulate the surface can also be formed. The isolated surface carbon atoms which are important in the filament formation dissolve into the nickel particle at the gas side, and diffuse to the rear, at the support side. At the front of the nickel particle, a selvedge with high concentration is created

because of the segregation behavior of carbon in nickel: the surface is enriched with carbon, and the carbon concentration decreases from the surface concentration to the bulk concentration of interstitially dissolved carbon over a number of atomic layers. The relation between the surface coverage of carbon and the bulk concentration of interstitially dissolved carbon in nickel, just below the selvedge, can be described by a segregation isotherm. The diffusion of carbon through the nickel particle is ascribed to the diffusion of interstitially dissolved carbon in nickel. A carbon filament precipitates at the support side of the nickel particle.

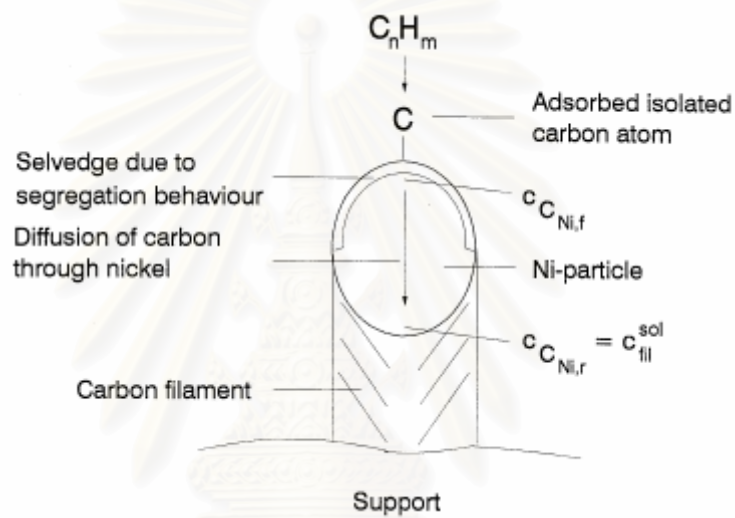


Figure 3.1 Schematic representation of mechanism of filamentous carbon formation

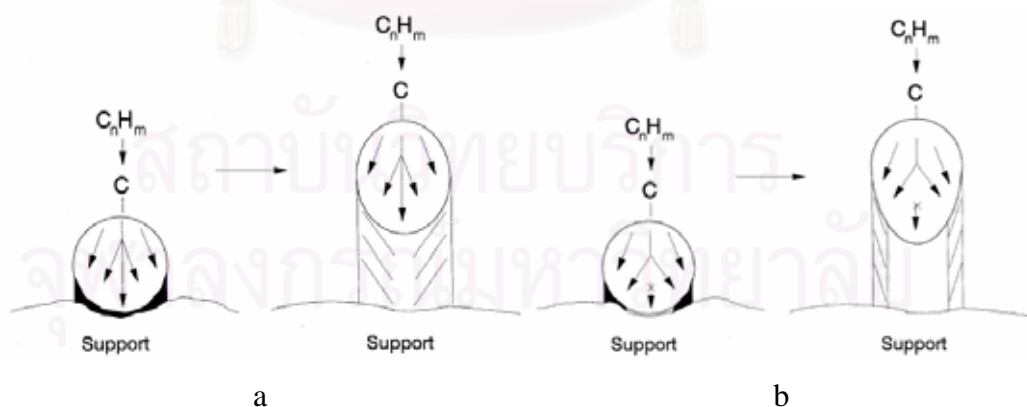


Figure 3.2 Schematic representation of the deformation of the metal particle

a) at low temperature/formation of full filaments

b) at high temperature/formation of hollow filaments.

At low temperature, the rate of nucleation is low compared to the rate of diffusion. Nucleation is uniform over the whole metal/carbon (or support) interface, and the particle is nicely lifted from the support when carbon layers are excreted. Full filaments are formed, without hollow channel.

At high temperature, nucleation is instantaneous, intrinsically much faster than the rate of diffusion. Nucleation occurs as soon as the supersaturation reaches the metal/support interface. The difference in diffusional path length causes rapid nucleation and excretion of carbon layers near the metal/gas interface, so that the metal is lifted from the support at these places. As soon as carbon excretion starts, the concentration of carbon in nickel drops sharply to the saturation concentration of filamentous carbon. Therefore, no driving force is present any longer for nucleation at places with high diffusional path lengths: no carbon excretion will take place there and hollow filaments are obtained.

CHAPTER IV

EXPERIMENTAL

This chapter explains the details of catalysts, experimental systems and experimental procedures used in the present work. It is divided into five main parts. Firstly, the details of catalyst, dilution material, and reactant gas are provided in sections 4.1. Section 4.2 describes the apparatus used for testing the reforming reaction. The reaction procedures are then given in section 4.3. The fourth part (section 4.4) explains the details of catalyst characterization by various techniques such as N₂ physisorption, TPR, CH₄-TPD, CO₂-TPD, BET surface area, SEM, XRD, and TPO. Lastly, section 4.5 describes the catalyst evaluation in term of catalytic activity measurement in the reforming reaction.

4.1 Chemicals and Materials

4.1.1 Catalyst

The catalyst used in the present work is Ni/SiO₂.MgO (commercial grade) obtained from Japan. This catalyst was applied in the carbon dioxide reforming of methane reaction. The shape of catalyst is solid cylindrical extrudate with a diameter of three millimeters and three millimeters in length. More details of this catalyst characteristics are presented in Table 4.1

Table 4.1 The specific properties of catalyst used in the experiment

Catalyst	Ni/SiO ₂ .MgO
Ni content	55 % w/w
Support/co-catalyst	SiO ₂ , MgO
Surface area [m ² /kg]	1.21 x 10 ⁵
Ni Surface area [m ² /kg]	8.37 x 10 ³
Ni diameter [nm]	44

4.1.2 Dilution material

A dilution material was used for uniformly mixing with catalyst before packing in the reactor in order to reduce the bed pressure drop due to carbon formation from the reaction and to reduce temperature gradients along the catalyst bed. Silicon dioxide (SiO_2) supplied by Fluka was chosen as a dilution material for this research. The average size of silicon dioxide was 40-100 mesh. The ratio of Ni/ SiO_2 .MgO catalyst to silicon dioxide was 0.3:1 used in the whole experiment.

4.1.3 Reactant gases

The details of gases used to study the reforming reaction are illustrated in Table 4.2

Table 4.2 Reaction gases used for the experiment

Gas	Grade	Supplier
Methane	Grade 4	TIG
Carbon dioxide	High pure	TIG
Hydrogen	Ultra high pure	TIG
Argon	Ultra high pure	TIG

4.2 Apparatus

Figure 4.1 shows the flow diagram of a lab-scale system, which was designed and constructed to study the gas phase carbon dioxide reforming of methane. The system consists of a catalytic reactor, an automatic temperature controller, an electrical furnace and a gas controlling system.

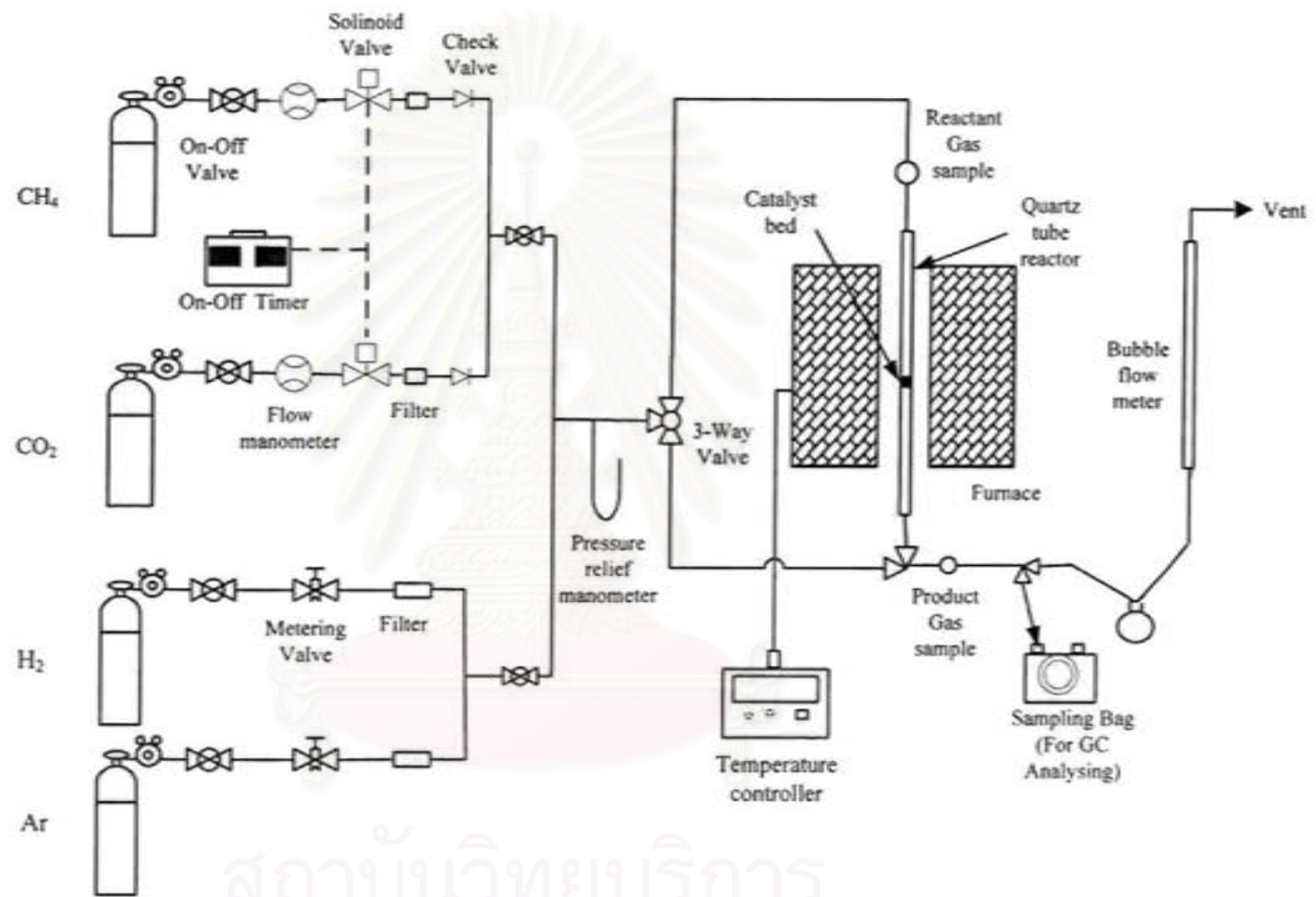


Figure 4.1 Schematic diagram of a lab-scale system to study carbon dioxide reforming of methane under periodic and steady state operation

4.2.1 Reactor

The reaction was performed in a conventional quartz tube with an inside diameter of 11 millimeters at atmospheric pressure. The quartz tube reactor was placed in the vertical direction with downward gas flow. There were two sampling points located before and after the catalyst bed. Catalyst was placed over a quartz wool, which was packed for supporting the catalyst bed.

4.2.2 Automatic Temperature Controller

This unit consists of a magnetic solid state relay switch connected to a variable voltage transformer and a temperature controller connected to a thermocouple. Reactor temperature was measured by thermocouple which was placed in the furnace at the position of the catalyst bed. The temperature control set point is adjustable within the range of room temperature to 1,000°C at the maximum voltage output of 220 V.

4.2.3 Electrical Furnace

The furnace with 2 kW heating coil was connected with the automatic temperature controller to supply heat to the reactor. The reactor could be operated from room temperature up to 750°C at the maximum voltage of 220 V.

4.2.4 Gas Controlling System

Each reactant gas was equipped with a pressure gas regulator (0-120 psig) and an on-off valve. The flow rate was controlled by mass flow controller (GFC17S) operated under the flow range between 0-50 mL/min. For periodic operation, each reactant feed was switched between opening and closing periodically by using a solenoid valve (Flon industry, Japan) controlled by a multi-timer (Sibata BT-3).

4.3 Experimental Procedure

The experiment was divided into 2 parts; steady operation and periodic operation.

For all samples, the catalyst was prepared by mixing 0.1314 g of Ni/SiO₂.MgO with 0.438 g of SiO₂. The mixture of catalyst was packed in the middle of the reactor and then placed in the electrical furnace. The reactor was heated up to 650°C under 30 mL/min of argon flow. When the temperature reached 650°C, the argon gas was switched off and the catalyst was reduced under 30 mL/min of hydrogen flow for 1 hour. After the catalyst reduction, the system was purged with argon again for 10 minutes to remove all hydrogen gas from the system. After that the reactor temperature was changed to desired values, those are 550°C, 650°C, 670°C, 690°C, 710°C, 730°C, and 750°C.

For steady operation, the reaction was started by introducing 12.5 mL/min CH₄ together with 12.5 mL/min CO₂ simultaneously. For periodic operation, the multi-timer was set to control the solenoid valves to allow 25 mL/min of CH₄ to pass through the reactor for 10 minutes and switch to 25 mL/min of CO₂ for 10 minutes. The operation occurred repeatedly until the end of experimental study.

The reaction was stopped at each setting reaction time. The reaction times used for operating were 90, 100, 190, and 200 minutes. The spent catalysts under periodic operation for any reaction temperatures and any reaction time were measured the weights, denoted, and collected for further before characterization. For example, the spent catalyst which was operated under periodic operation at 650°C for 190 minutes was denoted as "PO650C190".

Catalytic activities of the reaction were examined by a gas chromatography. Coke deposited on the spent catalysts were examined by various techniques including BET surface area, SEM, XRD, and TPO.

4.4 Reforming Reaction Study

After reaction, an effluent gas was sampled to analyze its composition. In case of steady state operation, product gas for each reaction time was sampled from the sampling point by a syringe. Whereas, in case of periodic operation, product gas for

every 10 minutes of each feeds was collected by using a sampling bag. A gas sample from the sampling bag was analyzed to determine the time-average composition of the product gas.

A gas chromatography Shimadzu modal 8A (GC-8A) equipped with a thermal conductivity detector (TCD) was used to analyze gas composition. Methane in feed stream, carbon monoxide and hydrogen in the product streams were analyzed using Molecular sieve 5A column. Carbon dioxide in the product stream was analyzed by using Poropak-Q column. The operating conditions for the gas chromatography are given in Table 4.3.

Table 4.3 Operating conditions of gas chromatograph for carbon dioxide reforming of methane

Gas Chromatograph	SHIMADZU FID GC 9A	
Detector	TCD	
Packed column	Molecular sieve 5A	Poropak-Q
- Column material	SUS	SUS
- Length (m)	2	-
- Outer diameter (mm)	4	-
- Inner diameter (mm)	3	-
- Mesh range	60/80	-
- Maximum temperature (°C)	350	-
Carrier gas	Ultra high purity Ar	Ultra high purity Ar
Carrier gas flow rate (mL/min)	30	30
Injector temperature (°C)	100	100
Detector temperature (°C)	100	100
Column temperature		
- initial (°C)	70	70
- final (°C)	70	70
Current (mA)	70	70
Analyzed gas	CH ₄ , H ₂ , CO	CO ₂

4.5 Catalyst Characterization

Various characterization techniques were used in this study in order to clarify the coke deposited on the spent catalysts at various reaction times and reaction temperatures from the carbon dioxide reforming of methane under periodic and steady state operations. The details of used techniques were listed as followed:

4.5.1 Temperature-programmed reduction (TPR)

The reduced temperature of the fresh catalyst was measured by using TPR technique determined by measuring the amount of hydrogen consumption in reducing catalyst using Micromeritics Chemisorb 2750. 0.2 g of sample was pre-treated in He (30 mL/min) at 250°C for 1 hour and then cooled down to room temperature. H₂ (20 mL/min) was switched into the sample while the system was heated at 10°C/min to 1000°C and detected by TCD. The calculation of amount of H₂ was done and reported by Chemisorp TPx software.

4.5.2 CH₄ temperature-programmed desorption (CH₄-TPD)

Adsorption ability of methane on the surface of the fresh catalyst were measured by using CH₄-TPD technique determined by measuring the amount of adsorbed methane on the surface using Micromeritics Chemisorb 2750. 0.3 g of sample was pre-treated in He (30 mL/min) at 250°C for 1 hour and then reduced in H₂ (30 mL/min) at 650°C for 1 hour for the purpose of adjusting the same condition to the catalyst before reaction. CH₄ (30 mL/min) was switched into the sample at room temperature for 1 hour and then He (30 mL/min) was fed to removed adsorbed CH₄ from the surface of catalyst while the system was heated at 10°C/min to 1000°C and detected by TCD. The calculation of amount of CH₄ was done and reported by Chemisorp TPx software.

4.5.3 CO₂ temperature-programmed desorption (CO₂-TPD)

The basic property and carbon dioxide adsorption ability on the surface of the fresh catalyst were measured by using CO₂-TPD technique determined by measuring the amount of adsorbed carbon dioxide on the surface using Micromeritics Chemisorb 2750. 0.3 g of sample was pre-treated in He (30 mL/min) at 250°C for 1 hour and reduced in H₂ (30 mL/min) at 650°C for 1 hour for the purpose of adjusting the same condition to the catalyst before reaction. Then CO₂ (30 mL/min) was switched into the sample at room temperature for 1 hour and then He (30 mL/min) was fed to removed adsorbed CO₂ from the surface of catalyst while the system was heated at 10°C/min to 1000°C and detected by TCD. The calculation of amount of CO₂ was done and reported by Chemisorp TPx software.

4.5.4 N₂ physisorption

The total surface area, pore volume and pore size of catalysts were calculated using a Micromeritics model ASAP 2020. The sample cell which contained 0.3 g of sample was placed into Micromeritics model ASAP 2020. After degassing step, N₂ physisorption were carried out for measuring the surface area and pore volume of catalyst.

4.5.5 Scanning electron microscopy (SEM)

Catalyst granule morphology and elemental distribution were obtained using a JEOL JSM-35F scanning electron microscope. The SEM was operated using the back scattering electron (BSE) mode at 20 kV at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University.

4.5.6 X-Ray Diffraction (XRD)

The crystallinity and structure of catalysts were analyzed by XRD analysis. The XRD analysis was performed by a SIEMENS D5000 X-ray diffractometer connected with a personal computer with Diffract AT version 3.3. The measurement

was carried out by using CuK_α radiation with Ni filter. The conditions of the measurement are shown as followed:

2θ range of detection = 10-80°

Resolution = 0.04°

Number of scan = 20

4.5.7 Temperature-programmed oxidation (TPO)

Temperature-programmed oxidation was used to study the amount of coke deposited on the catalysts. The operation was performed by using Micromeritics Chemisorb 2750. Most amount of sample after the reaction was pre-treated in He (25 mL/min) at 250°C for 1 hour for eliminating moisture from the catalyst and cooled down to room temperature. Then 1 vol% oxygen in helium (15 mL/min) was switched into the sample while the system was heated at 10°C/min to 1000°C and detected by TCD detector. The calculation of amount of CO_2 in the effluent gas was analyzed and reported by Chemisorp TPx software.



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CHAPTER V

RESULTS AND DISCUSSION

The study was conducted in order to investigate the reforming activity and the degree of coke deposited on Ni/SiO₂.MgO catalyst from carbon dioxide reforming of methane under both periodic and steady state operations. The results in this chapter are divided into three main parts. The first part describes the characteristics of commercial Ni/SiO₂.MgO catalyst which was used in this study. In the second part, the catalytic activities at various reaction temperatures of the reaction under periodic operation were investigated comparing with those under steady state operation. The last part describes the characteristics of the catalysts after the reaction at various reaction times and temperatures. The degree of coke formation is also discussed in this part.

5.1 Characterization of Fresh Ni/SiO₂.MgO Catalyst

The characterizations which give useful information of characteristics of the catalyst were investigated as following.

5.1.1 Temperature-programmed reduction (TPR)

Temperature programmed reduction (TPR) of fresh Ni/SiO₂.MgO catalyst was performed in order to investigate the suitable reduction temperature for reducing the metal oxide catalyst to metallic catalyst, in which provides higher reforming activity. TPR profile of the fresh catalyst is shown in Figure 5.1. For this catalyst, three reduction peaks were observed at 190, 616, and 813°C. The strongest peak which was observed at 616°C can be assigned to the reduction of Ni species with strong interaction with silicon dioxide support. The peak at 813°C is assigned to the reduction of Ni species with strong interaction with magnesium oxide. In our experiment, the temperature 650°C was used for reduction of catalyst with hydrogen. Under this condition, metallic nickel was formed in the reduction step. Thus, the

catalyst phase was converted from nickel oxide to metallic nickel which is more active before the reaction.

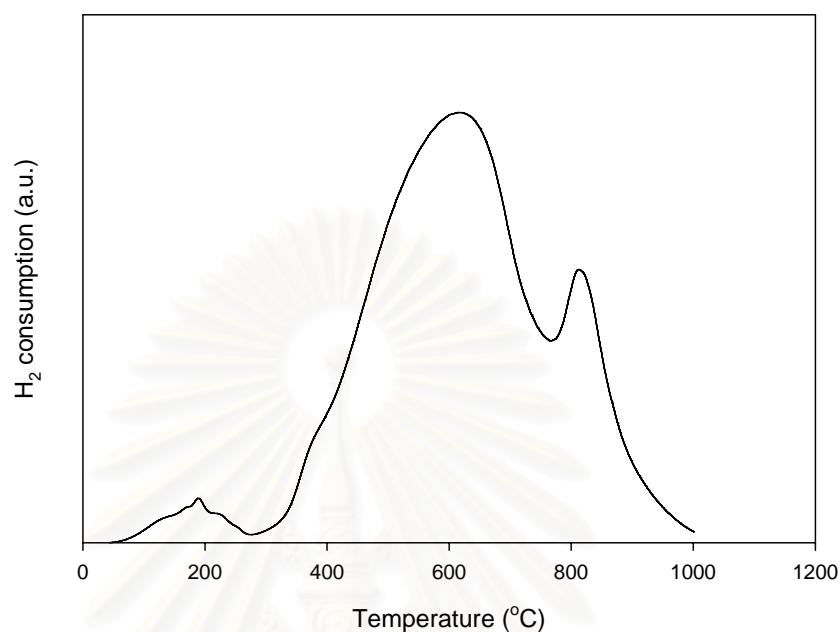


Figure 5.1 Temperature-programmed reduction profile of fresh catalyst

5.1.2 CH₄ temperature-programmed desorption (CH₄-TPD)

CH₄ temperature-programmed desorption (CH₄-TPD) of fresh catalysts was carried out in order to obtain an information about methane adsorption behavior on the catalyst samples. The samples were reduced in H₂ at 650°C for 1 h prior to adsorption of CH₄ and then the adsorbed catalysts were purged with He at the same adsorption temperature to remove physisorption. The results are shown in Figure 5.2. The profile shows that methane can adsorb on the surface of the Ni/SiO₂.MgO catalyst at temperature range 600-1000°C. From our reaction, reaction temperatures were ranged at 650-750°C. It was found that the methane adsorption on the catalyst at reaction temperature 750°C is higher than that at 650°C, thus, the methane conversion at 750°C should be higher than that at 650°C.

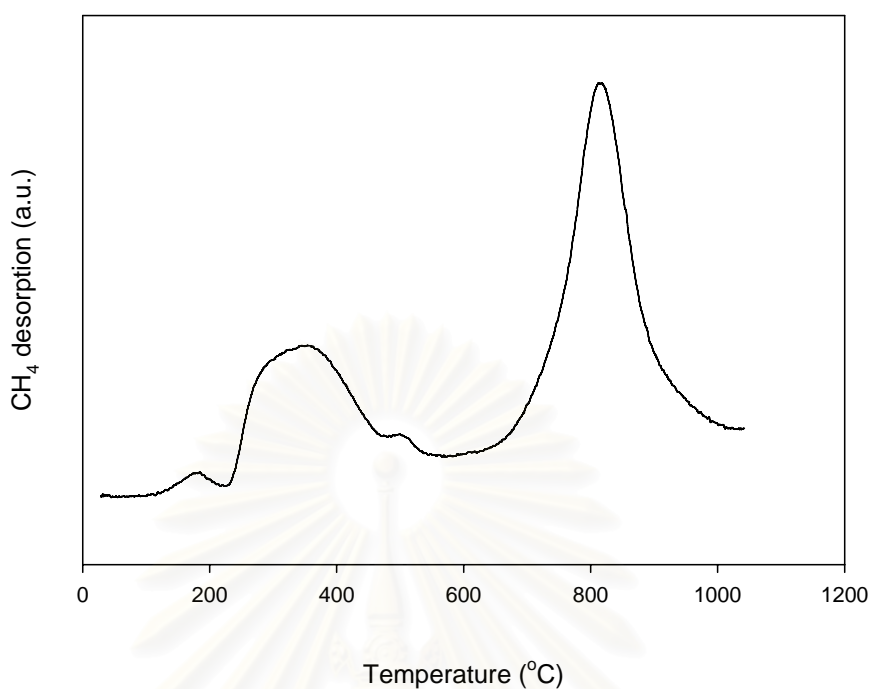


Figure 5.2 CH₄ temperature-programmed desorption profile of fresh catalyst

5.1.3 CO₂ temperature-programmed desorption (CO₂-TPD)

The effect of the surface basicity of the catalysts was studied by CO₂-TPD. The CO₂-TPD profile of Ni/SiO₂.MgO is presented in Figure 5.3. Two peaks were presented at 150 and 815°C. The first peak at low temperature may be attributed to the desorption of the adsorbed CO₂ on weak basic site, while the second peak may be attributed to strong basic site of the catalyst. It was proposed that basic property of catalyst improves activity of CO₂ reforming reaction. The CO₂-TPD result of this catalyst was viewed as the ability of CO₂ adsorption on the catalyst surface. It was found that CO₂ adsorption at 750°C can be taken place well than those at 650°C alike to methane adsorption. Thus, the activity of this catalyst in carbon dioxide reforming of methane would prefer higher temperature.

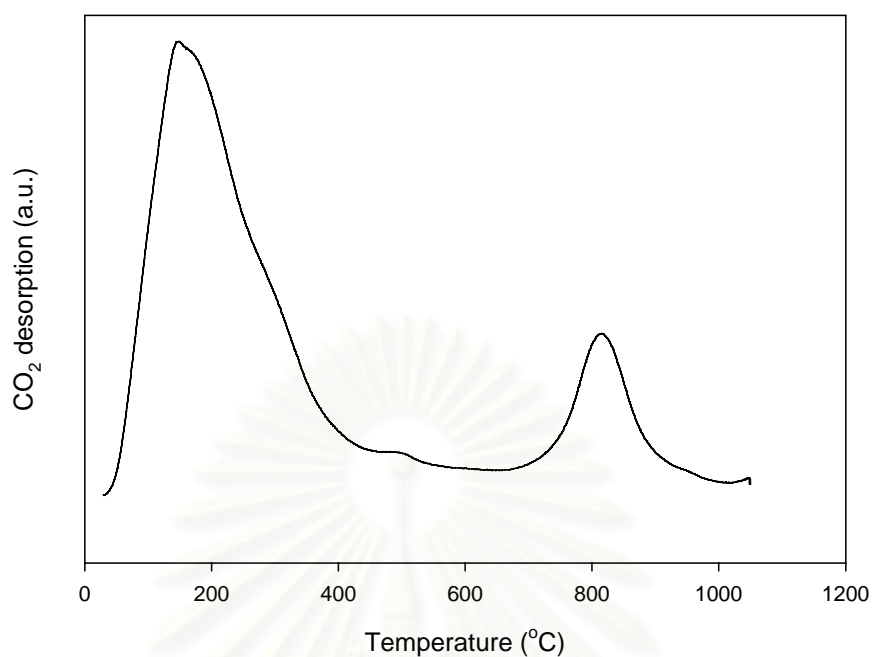


Figure 5.3 CO₂ temperature-programmed desorption profile of fresh catalyst

5.1.4 N₂ physisorption

N₂ physisorption was carried out by Micromeritics model ASAP 2020. The result of N₂ physisorption provides the information about surface area, pore volume, and pore size of the catalyst. The details of the result are given in Table 5.1. It can be seen that the BET surface area, pore volume, and pore size of fresh Ni/SiO₂.MgO are 121.43 m²/g, 0.18 cm³/g, and 59.52 Å respectively. As seen in Figure 5.4, this catalyst has pore diameter distribution in mesopore range (with the range of 20-100 Å) in terms of surface area measured by BJH accumulated desorption.

Table 5.1 Results from N₂ physisorption of fresh catalyst

Surface Area and Porosity Analyzer	Amount
Surface area	
- Single point surface area at P/Po = 0.199761363	119.24 m ² /g
- BET Surface Area	121.43 m ² /g
- Langmuir Surface Area	164.80 m ² /g
- t-Plot Micropore Area	25.50 m ² /g
- t-Plot External Surface Area	95.93 m ² /g
- BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å diameter	119.81 m ² /g
- BJH Desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å diameter	136.42 m ² /g
Pore Volume	
- Single point adsorption total pore volume of pores less than 1219.3097 Å at P/Po = 0.983863551	0.1797 cm ³ /g
- Single point desorption total pore volume of pores less than 687.1086 Å at P/Po = 0.971012876	0.1807 cm ³ /g
- t-Plot micropore volume	0.0111 cm ³ /g
- BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter	0.1873 cm ³ /g
- BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å diameter	0.1929 cm ³ /g
Pore Size	
- Adsorption average pore width (4V/A by BET)	59.21 Å
- Desorption average pore width (4V/A by BET)	59.52 Å
- BJH Adsorption average pore diameter (4V/A)	62.54 Å
- BJH Desorption average pore diameter (4V/A)	56.56 Å

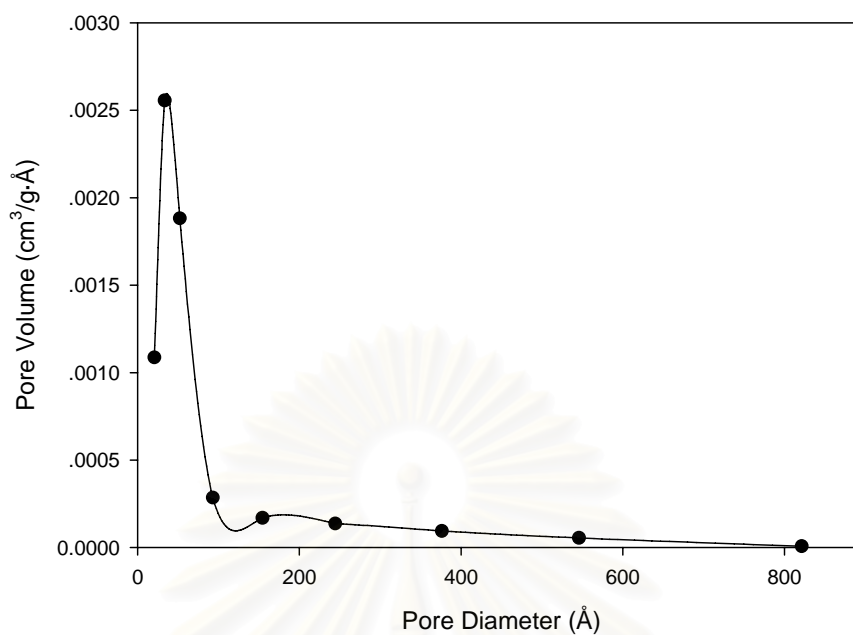


Figure 5.4 Pore distribution of fresh catalyst

5.1.5 Scanning electron microscopy (SEM)

The SEM technique is useful for judging the surface structure of the sample. The surface morphology of nickel oxide on silica support is exhibited by SEM image of fresh Ni/SiO₂.MgO catalyst as shown in Figure 5.5.

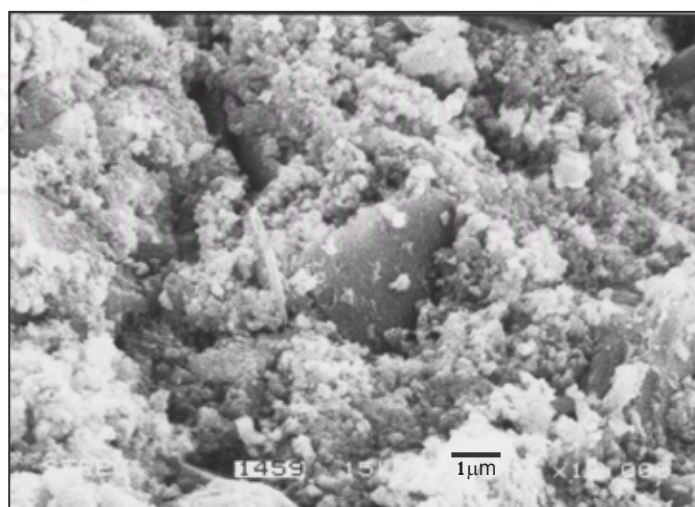


Figure 5.5 SEM micrograph of fresh catalyst

5.2 Catalytic Activity in Carbon Dioxide Reforming of Methane

In this part, the behaviors of the carbon dioxide reforming of methane over Ni/SiO₂.MgO catalyst under periodic and steady state operations were investigated. For periodic operation, the operation consists of two main steps: (i) methane cracking by feeding methane solely and (ii) regeneration of catalyst via reverse Boudouard reaction by feeding carbon dioxide. For steady state operation, the operation was carried out by feeding methane and carbon dioxide simultaneously. It should be noted that the total flow rates of feeds for both operations were identical. The methane conversion, carbon dioxide conversion, and hydrogen yield for both operations were investigated at several reaction temperature in the range of 650-750°C. The results of activities under periodic operation were shown in Figures 5.6-5.8 whereas those under steady state operation were shown in Figures 5.9-5.11.

The methane conversion under periodic operation at several temperatures is shown in Figure 5.6. At 750°C, Ni/SiO₂.MgO catalyst showed high conversion of methane about 67% at the beginning but it declined rapidly to 27% when operated for 240 minutes. Inversely, conversion of methane at reaction temperature 650°C started at about 48% and remains constant after exposure for 240 min. For other reaction temperatures between 670-730°C, methane conversions were obtained as the same trend. That is, at higher temperature, methane conversion was obtained at high value at the beginning of reaction and decreased continuously with increasing reaction time, whereas at lower temperature, methane conversion was almost constant throughout reaction time.

The carbon dioxide conversion under periodic operation is shown in Figure 5.7. Similar trend as methane conversion were observed; it was found that the carbon dioxide conversion at reaction temperature of 750°C decreased from about 55% at the beginning to about 24% at reaction time 240 minutes, whereas at reaction temperature of 650°C, carbon dioxide conversion was nearly constant at 35%. For hydrogen yield, the selectivity of methane is considered to equal to 100% due to stoichiometry. The hydrogen yield equals to the methane conversion. Thus, it was presented in the same trend.

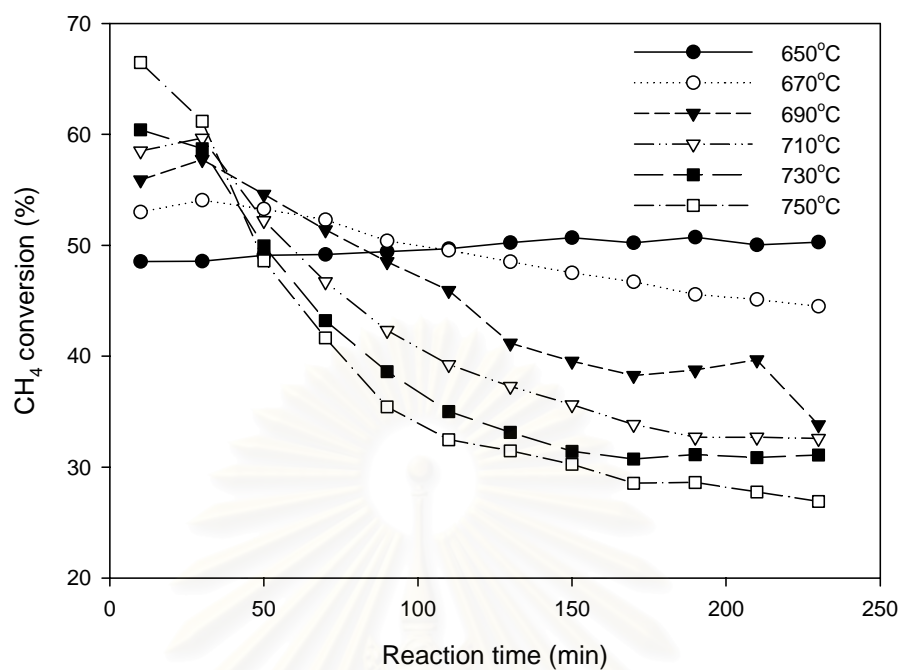


Figure 5.6 Methane conversion in carbon dioxide reforming of methane reaction under periodic operation at different reaction temperatures

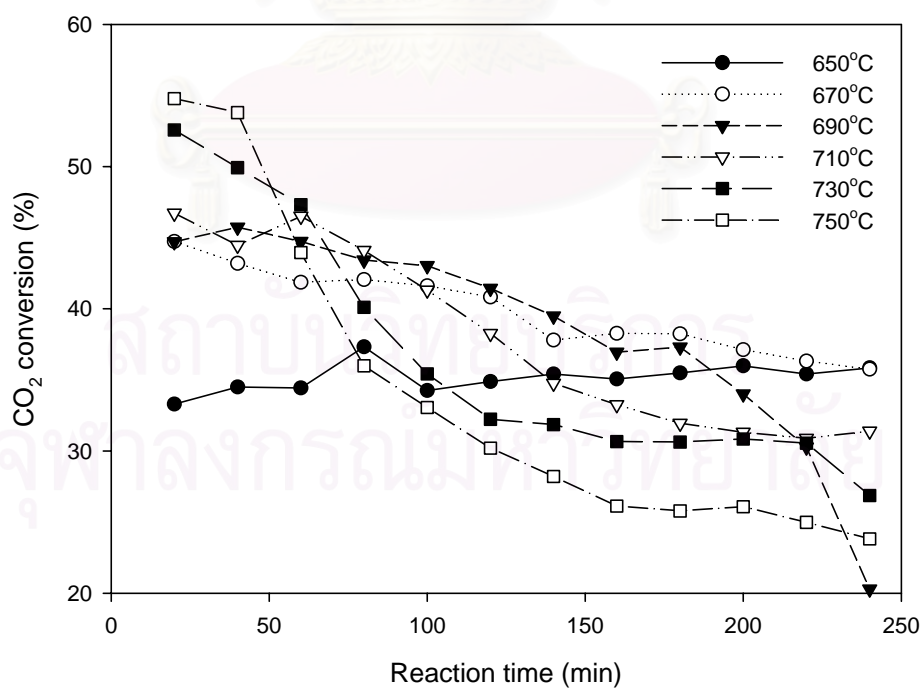


Figure 5.7 Carbon dioxide conversion in carbon dioxide reforming of methane reaction under periodic operation at different reaction temperatures

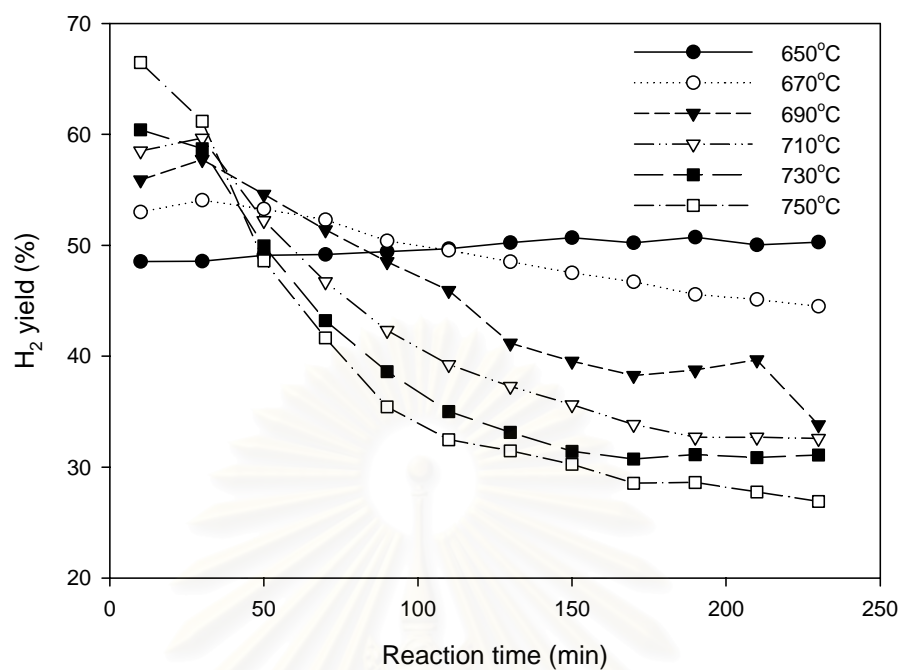


Figure 5.8 Hydrogen yield in carbon dioxide reforming of methane reaction under periodic operation at different reaction temperatures

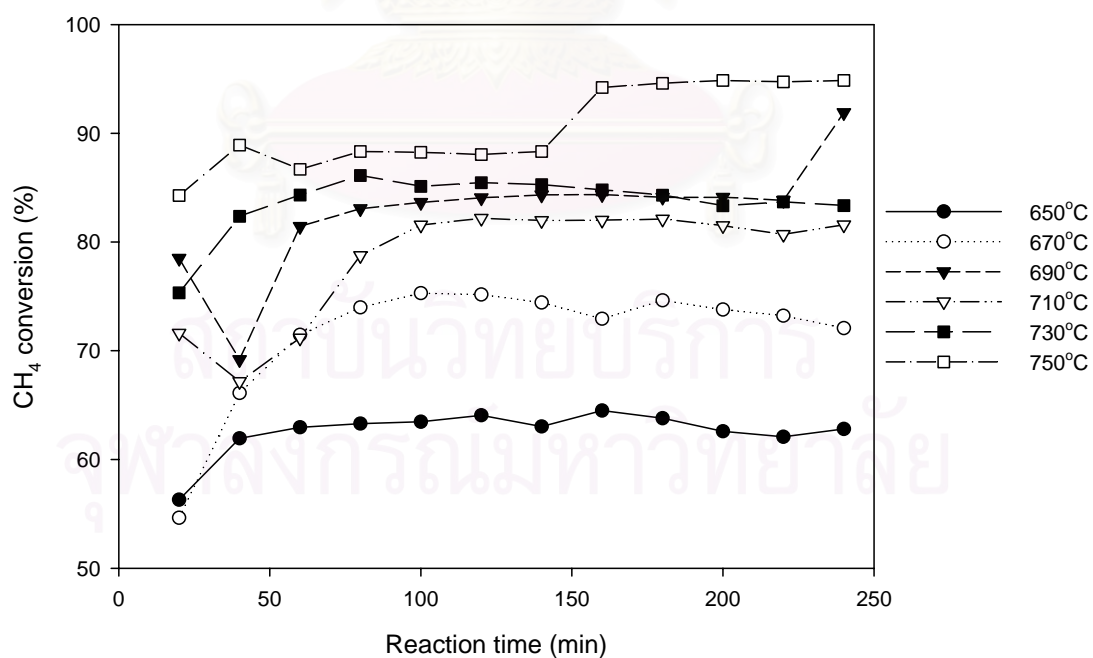


Figure 5.9 Methane conversion in carbon dioxide reforming of methane reaction under steady state operation at different reaction temperatures

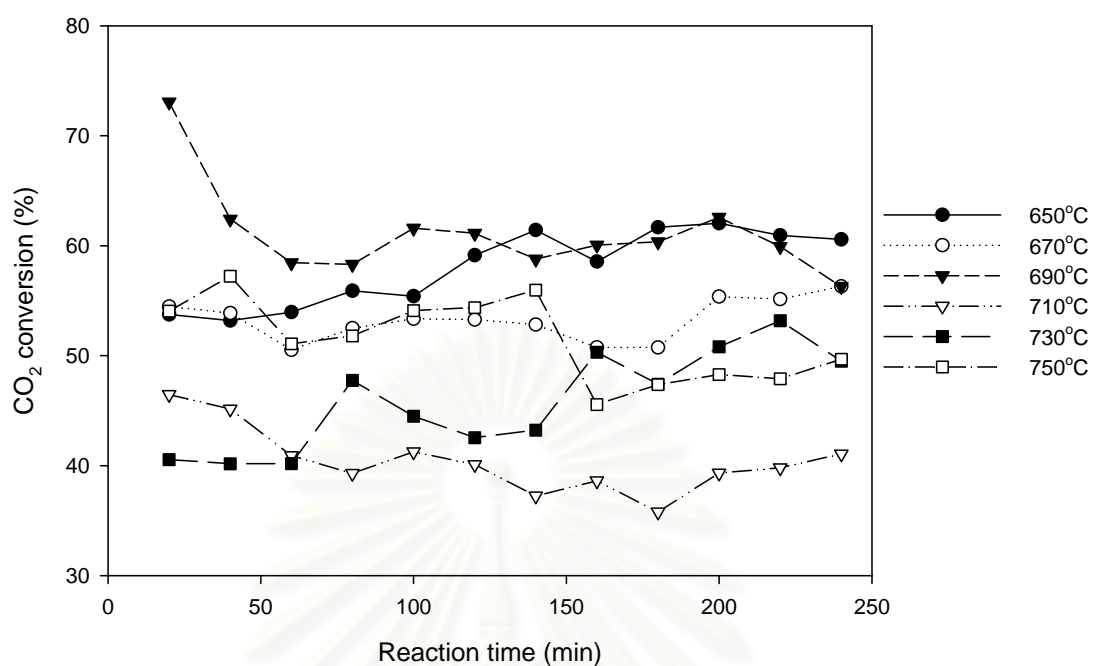


Figure 5.10 Carbon dioxide conversion in carbon dioxide reforming of methane reaction under steady state operation at different reaction temperatures

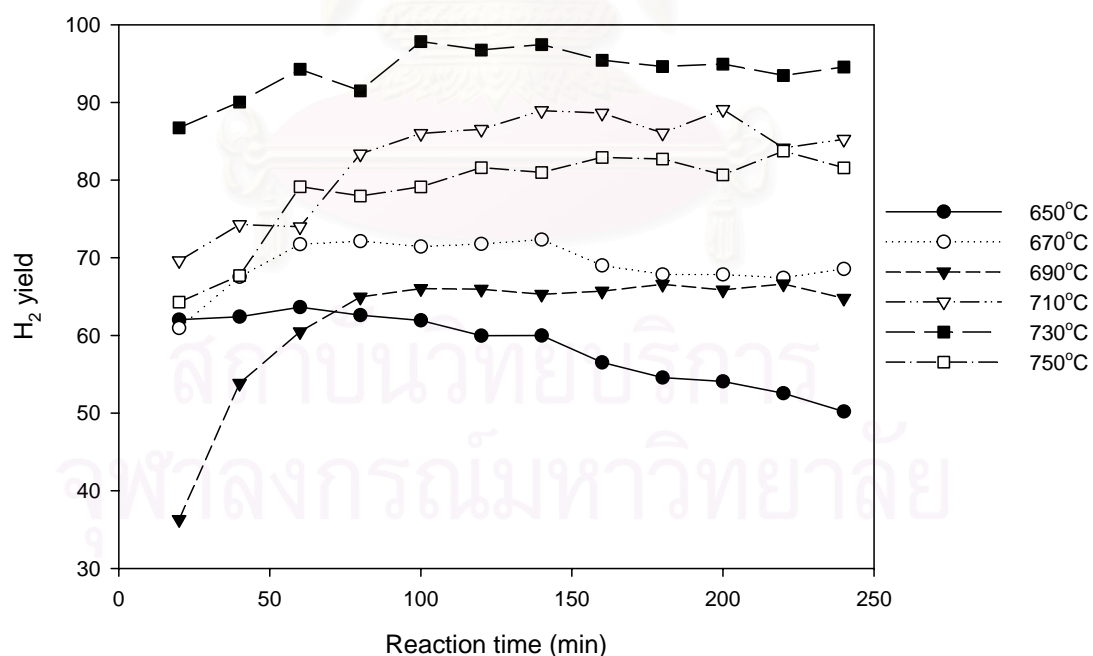
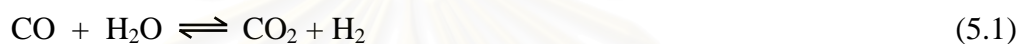


Figure 5.11 Hydrogen yield in carbon dioxide reforming of methane reaction under steady state operation at different reaction temperatures

Under steady operation, as shown in Figure 5.9, methane conversion did not decrease with increasing reaction time for all operating temperatures. After exposure for 240 min, the methane conversions at reaction temperatures 650, 670, 690, 710, 730, and 750°C were 63, 73, 83, 81, 84, and 90% respectively. Methane conversions for steady state operation tended to be constant with reaction time and to increase with increasing reaction temperature. As shown in Figure 5.10, carbon dioxide conversions and hydrogen yield tended to be constant with reaction time but did not tend clearly with reaction temperature. It offered the highest and lowest conversions at reaction temperatures 690 and 710°C respectively. This is probably affected by the occurrence of the reverse water-gas shift reaction.



Therefore, the amount of carbon dioxide increases in product and the conversion slightly decreases. Hydrogen conversion under steady operation also tended similar to methane conversion.

By the comparison periodic operation with steady state operation for carbon dioxide reforming of methane at range of reaction temperature 650-750°C, it was found that Ni/SiO₂.MgO catalyst showed stability under steady state operation. Unlikely, under periodic operation, the catalyst showed stability only at low temperature but showed decline of activity over reaction time at high temperature. These results correspond to the previous study (Promaros *et al.*, 2007). It has been suggested that different kinds of coke formation on the catalyst at different temperatures may affect on catalytic activity of this catalyst under periodic operation. For further investigations, characterization of used catalysts after exposure in periodic operation at different reaction temperatures and reaction times were carried out. The details are mentioned in the next section.

5.3 Characterization of Spent Catalysts

In this section, characteristics of spent catalysts by emphasizing on coke deposited on the catalyst surface were studied. The carbon dioxide reforming of methane was carried out under periodic operation by alternating feed between

methane and carbon dioxide every 10 minutes. Reaction temperature varied in the range 650-750°C. Four values of reaction times (90, 100, 190, and 200 min) were considered. The reaction times 90 and 190 min stand for the used catalyst after methane cracking period, whereas the reaction times 100 and 200 min stand for the used catalyst after regeneration with carbon dioxide. Various techniques were applied to investigate the formation of carbon species on the surface on the surface of catalyst including BET surface area measurement, SEM, XRD, and TPO.

5.3.1 Degree of Coke formation on the surface of spent catalysts

In order to understand the behavior of coke formation, two operating parameters, reaction temperature and reaction time, were considered simultaneously. Figure 5.12 shows the weights of catalyst before and after reaction, it is clearly seen that reaction temperature and reaction time affected to change in the weight of catalyst. It should be noted that the weight change theoretically obtained from coke formation on the surface of the catalyst.

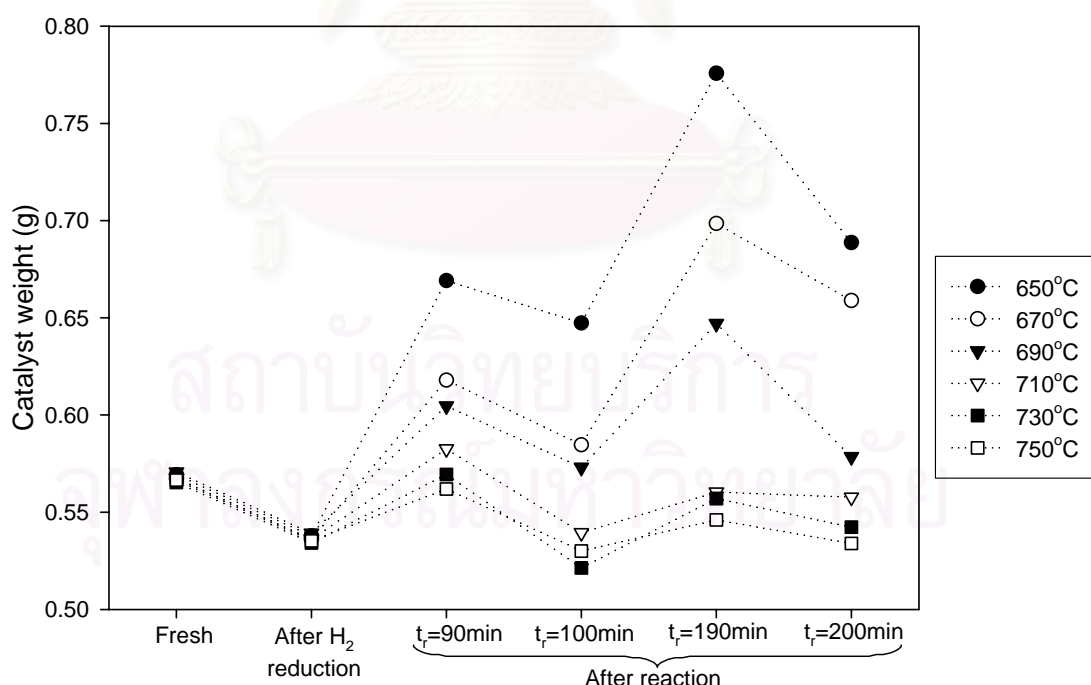


Figure 5.12 Catalyst weights before and after reaction

At the beginning, the catalyst was reduced with hydrogen to form metallic phase of nickel species. The weight of reduced catalyst decreased about 5.5%. Then the reforming reaction under periodic operation started. The weights of used catalysts were examined at reaction time 90 min which was the time ending methane cracking period. It was found that, at higher reaction temperature, lower coke formation was observed in the system. After that, at the reaction time 100 min, the catalyst weights after regeneration period were examined. It was found that, at lower reaction temperature, higher coke was formed in the system. Similar trends were occurred at reaction times of 190 and 200 min. These results were in the opposite to the result of investigating conversions in previous part, in which the CH₄ and CO₂ conversions decreased with increasing reaction temperature. Thus, the phenomena were possible affected by the type of coke deposited at different reaction temperatures.

From the BET study over catalyst at different conditions as shown in Table 5.2, it was found that reaction temperature and reaction time also affect the surface area of catalyst. The BET surface area of fresh catalyst is 104.62 m²/g. Reduction of catalyst with hydrogen decreases the BET surface area to 46.96 m²/g but offered more active catalyst phase to the reforming reaction. In order to investigate the effect of temperature on BET surface area, the fresh catalyst was calcined in air at 750°C for 3 hours. It was found that high temperature dramatically affected on BET surface area of this catalyst. This result was due to sintering of catalyst. Therefore, the higher reaction temperature was used, the lower BET surface area was achieved. Amount of coke formed also affected on surface area of catalyst. At low temperature, BET surface areas increased from value of reduced catalysts after methane cracking period and decreased after regeneration with carbon dioxide. Nevertheless, at high temperature, BET surface areas were influenced by the effect of sintering more than effect of amount of coke formed. Thus, BET surface areas of cracking period were less than those of reduced catalyst. However, the value decreased after regeneration period similarly to the value at low temperature.

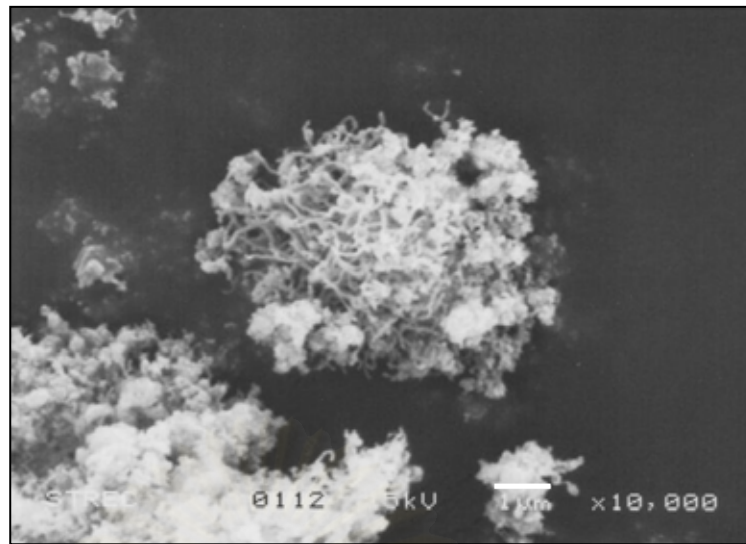
Table 5.2 BET surface areas of catalysts at different conditions

Catalysts		Surface area (m ² /g)			
Fresh		104.62			
After reduction with hydrogen at 650°C		46.96			
After calcination in air at 750°C 3 hr		45.43			
After reaction at		reaction time			
reaction temp.		90 min	100 min	190 min	200 min
650°C		56.24	60.51	76.56	64.99
670°C		33.94	50.11	78.24	51.69
690°C		47.77	33.56	65.52	59.07
710°C		47.89	35.95	32.30	18.55
730°C		31.24	20.97	17.94	14.54
750°C		20.74	19.36	20.42	14.06

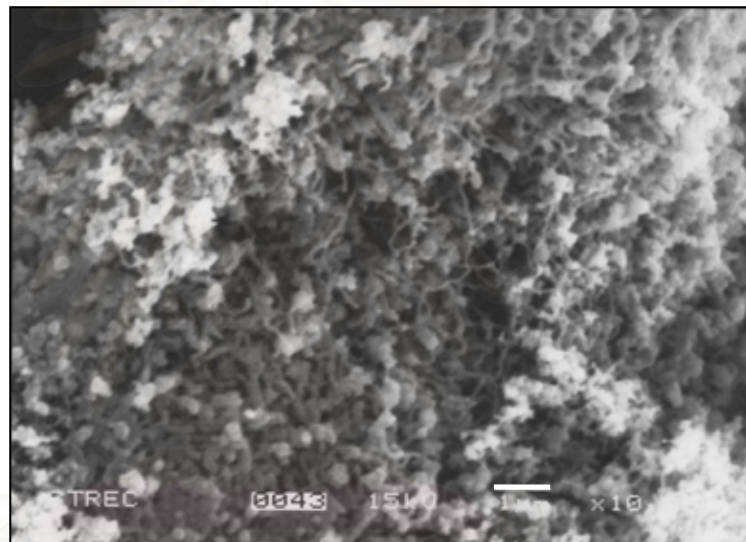
The SEM micrographs of used catalysts at reaction temperatures 650-750°C are shown in Figures 5.13(a)-5.13(f). All samples were tested after exposure in the reaction for 190 minutes, which was the ending time of methane cracking period. It can be seen that carbon formation in carbon dioxide reforming of methane presented the structure of filamentous carbon on the surface of catalyst at the reaction temperature range 650-750°C. From literature data, it was found that the formation of this type of carbon induced a serious pressure drop in the reactor (Takano *et al.*, 1994). Other type of carbon which was expected to form at these temperatures is the encapsulated carbon. It was believed that the encapsulated carbon could affect to stability of catalyst. Nevertheless, it is difficult to prove the formation of encapsulated carbon by SEM micrograph.

From SEM result, filamentous carbon was found on the surface of catalyst for all reaction temperatures. It was also found that when the high temperature was employed, the larger particle size of filamentous coke was observed.

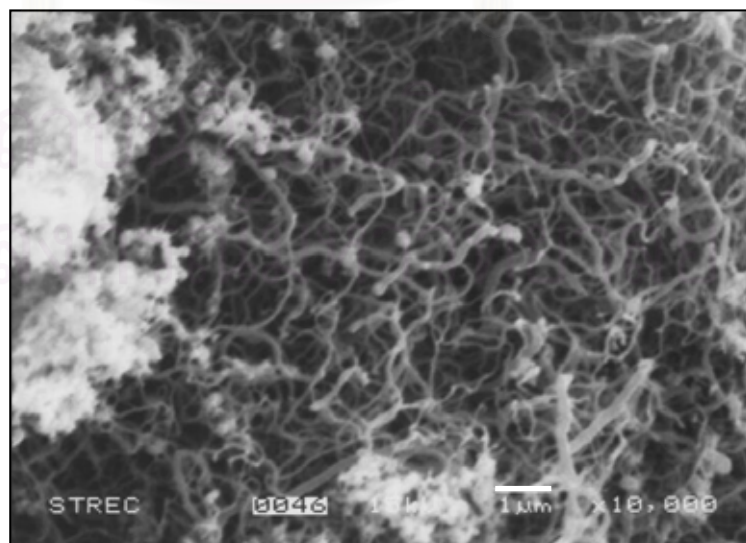
(a)



(b)



(c)



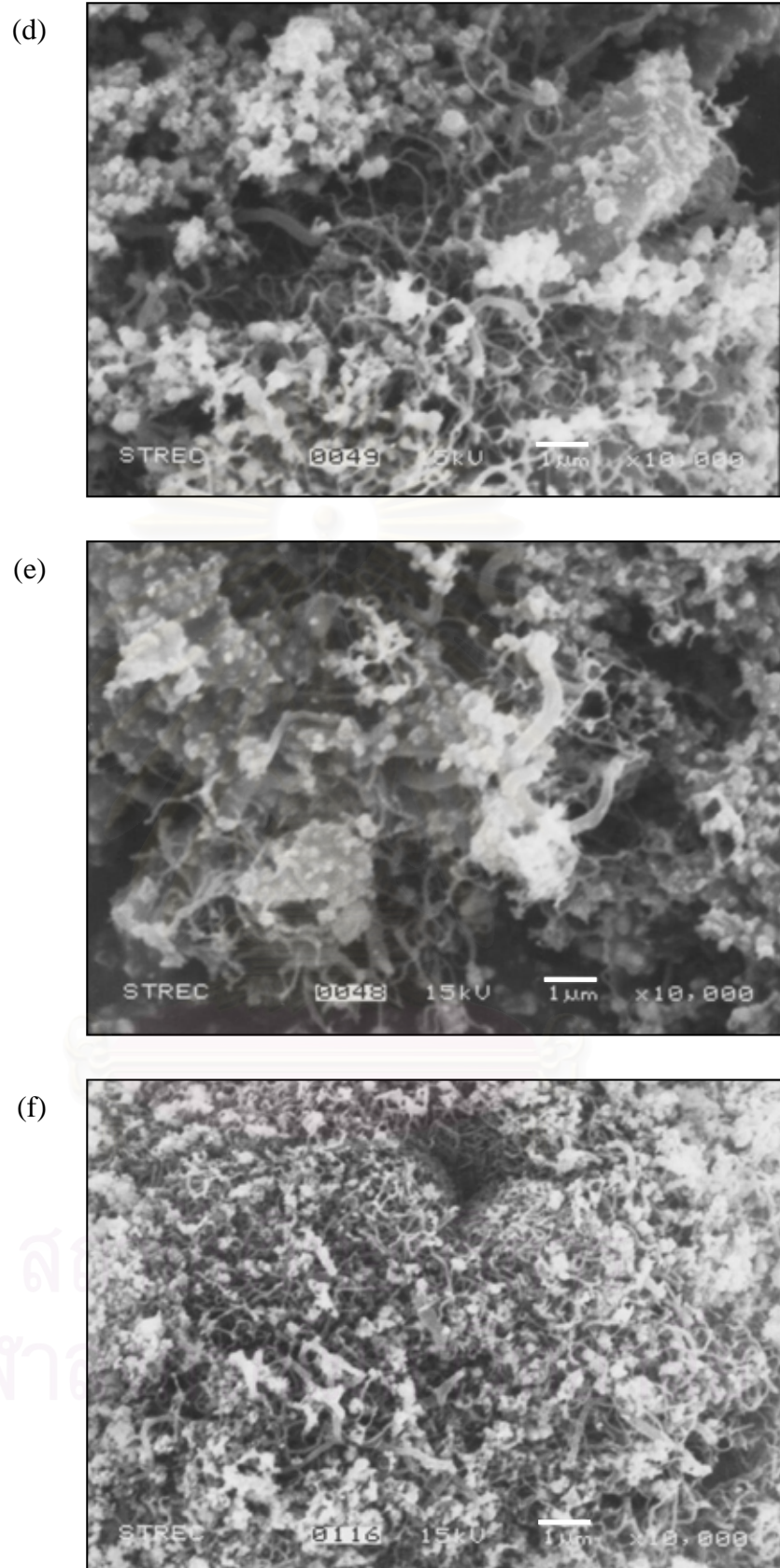
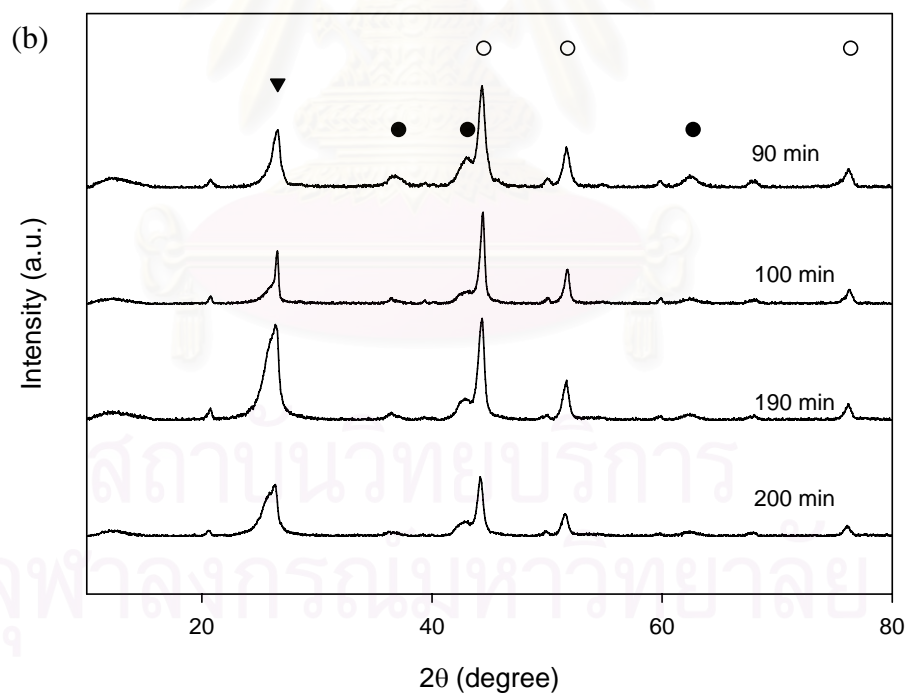
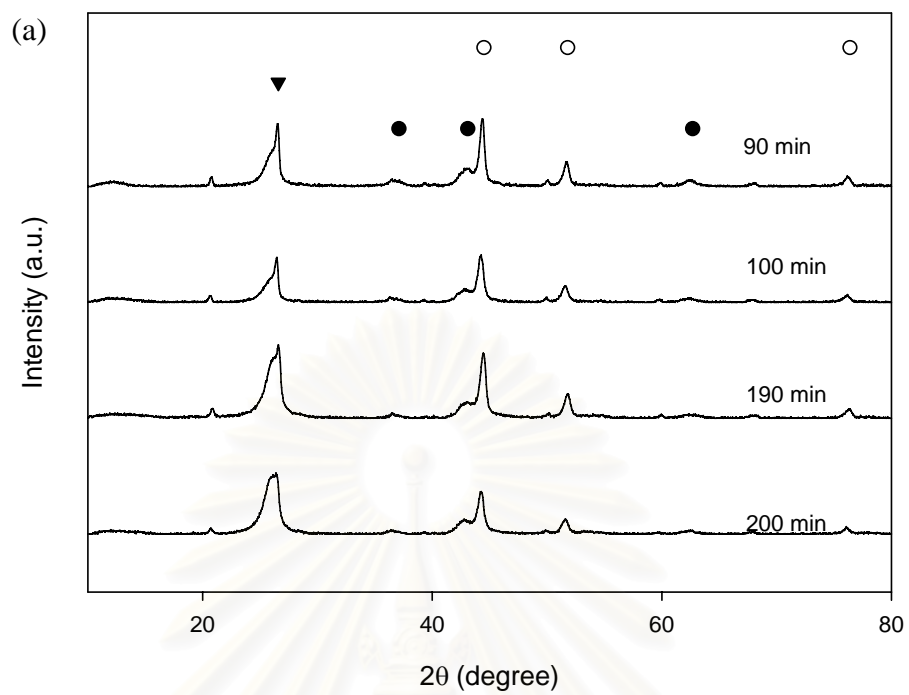
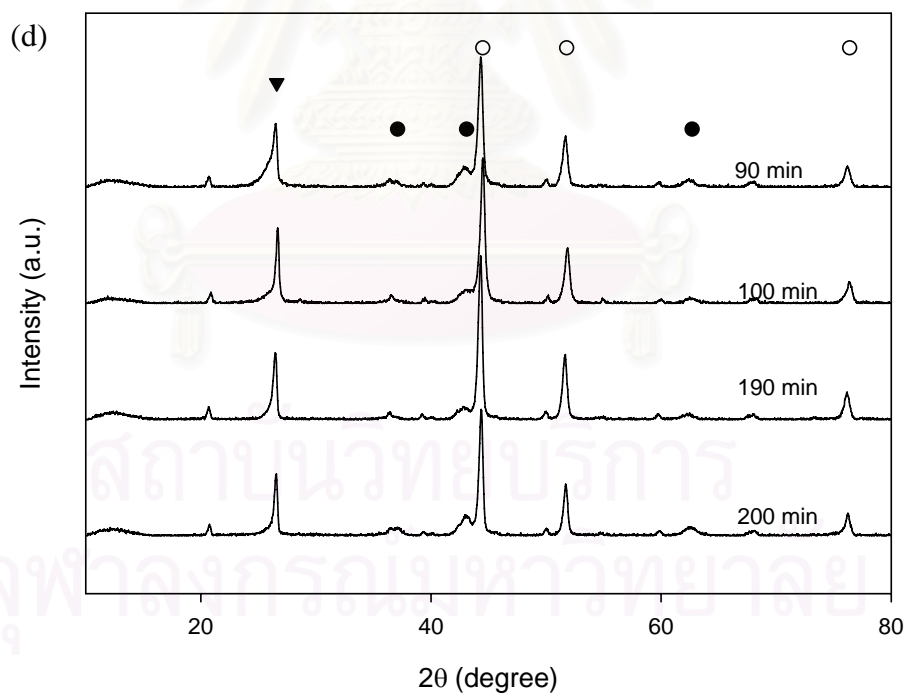
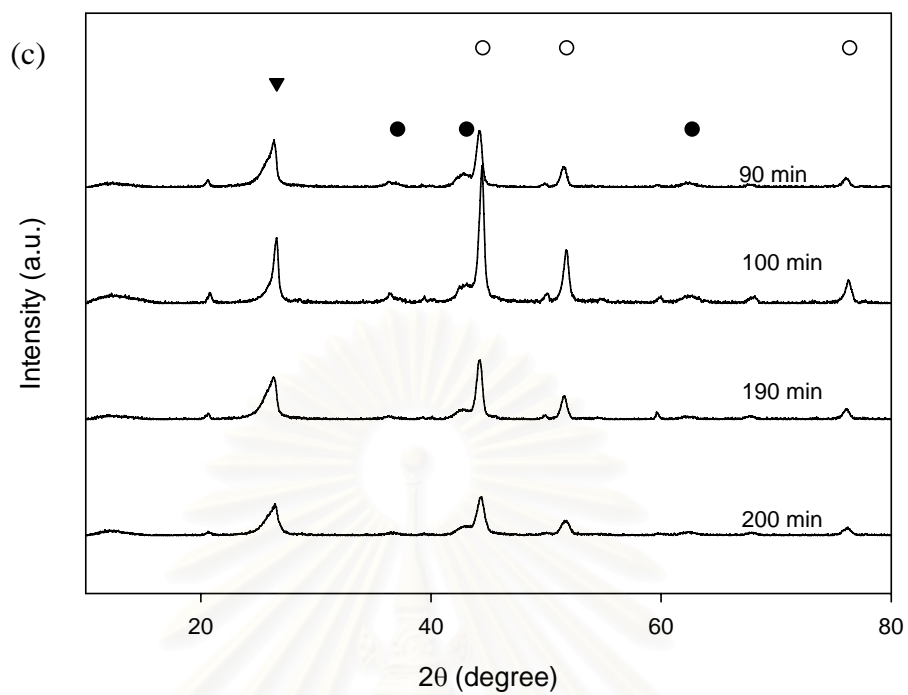


Figure 5.13 SEM micrographs of used catalysts at reaction time = 190 minutes and different reaction temperatures (a) at 650°C (b) at 670°C (c) at 690°C (d) at 710°C (e) at 730°C (f) at 750°C

The XRD patterns of used catalysts at reaction temperature range of 650-750°C are shown in Figure 5.14(a)-5.14(f). These patterns presented evidently the same strong peaks at $2\theta = 26.6$ and 44.5° and several low intensity peaks at certain degrees for all samples. The peak at $2\theta = 26.6^\circ$ was attributed to be the coke deposited on the surface of the catalyst. The presence of main structure of metallic Ni showed peaks at $2\theta = 44.5$, 51.8 , and 76.4° . The crystal structure of NiO was also observed for low intensity peaks at $2\theta = 37.1$, 43.1 and 62.7° . For tendency, higher and sharper intensity peaks of coke and Ni were found while reaction temperature was higher.

This XRD results indicated that there were the differences of particle sizes of catalyst for any reaction temperatures. The d-spacing of nickel and coke were calculated by using Scherrer equation as shown in Table 5.3. The d-spacing of nickel was obtained from peak at 44.5° whereas d-spacing of coke was obtained from peak at 26.6° . It was found that the higher temperature was used, the higher d-spacing for both nickel and coke were obtained. This was due to the effect of sintering of catalyst. This result was corresponding to the result of BET surface area because high value of d-spacing induced size of particle to be larger and lessened BET surface area. It should be noted that the d-spacing increased after regeneration with carbon dioxide and decreased after methane cracking in the next cycle. High values of d-spacing for both nickel and coke caused the blockage of active site of catalyst. Thus, it was probable to bring to the loss of stability of catalyst.





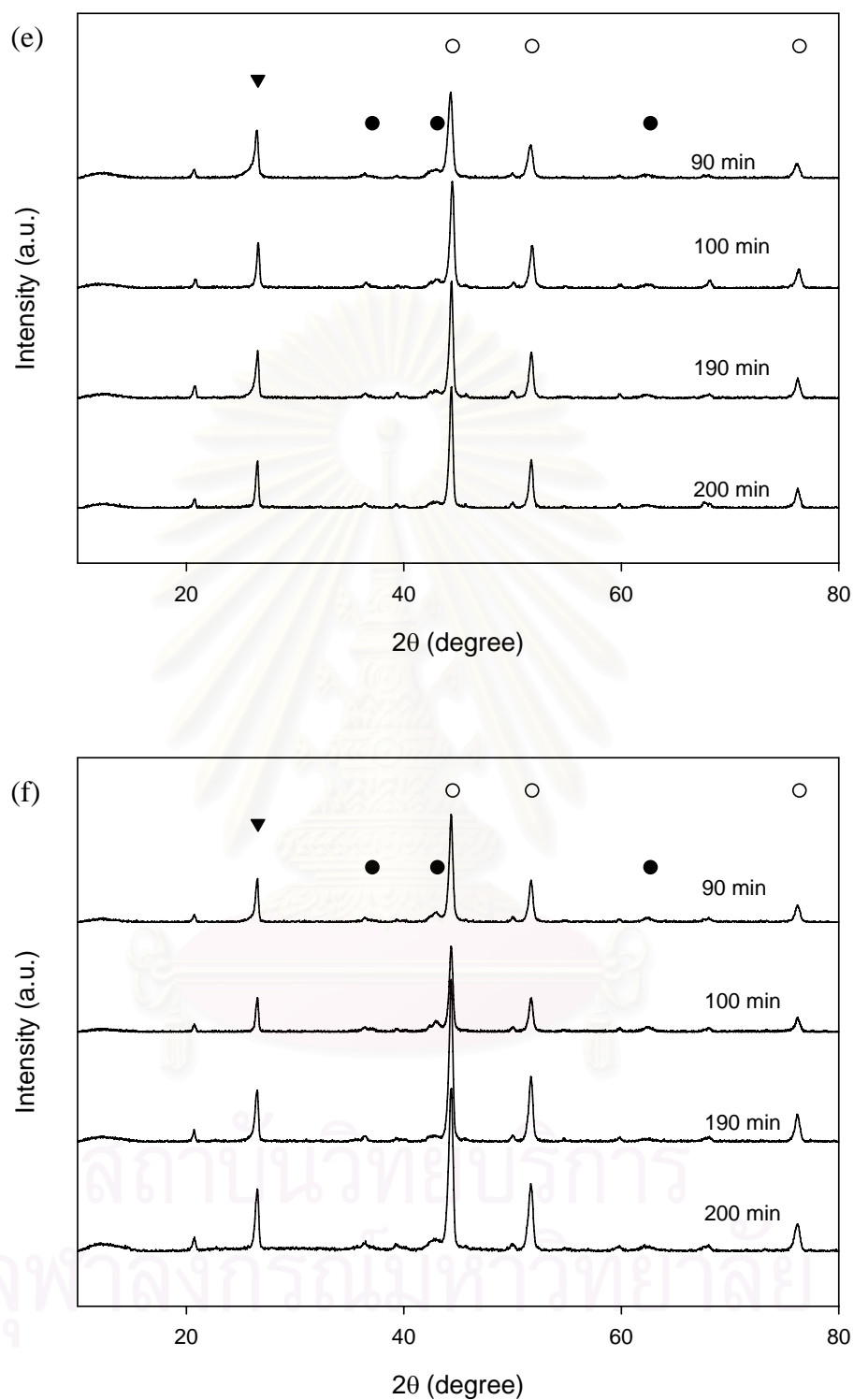
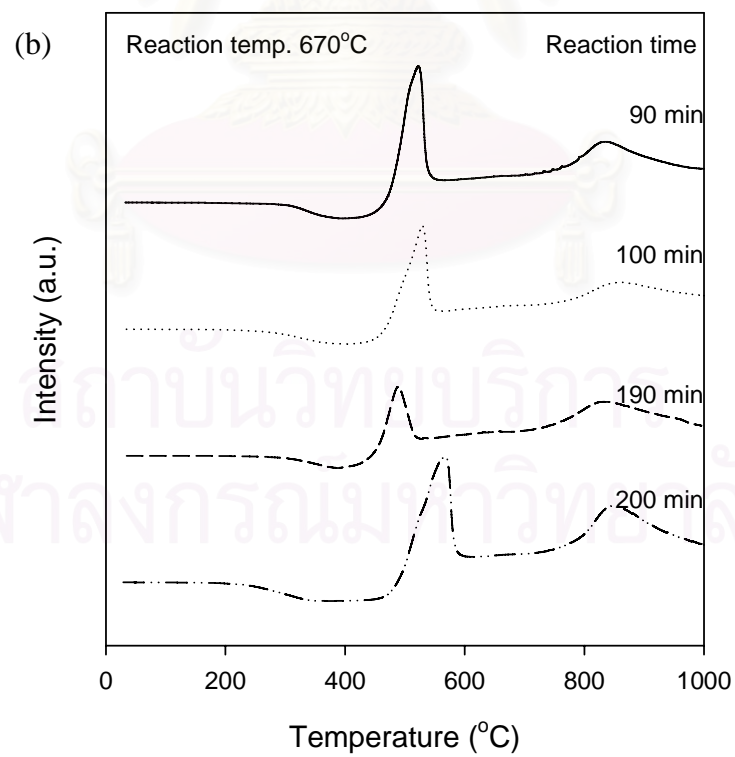
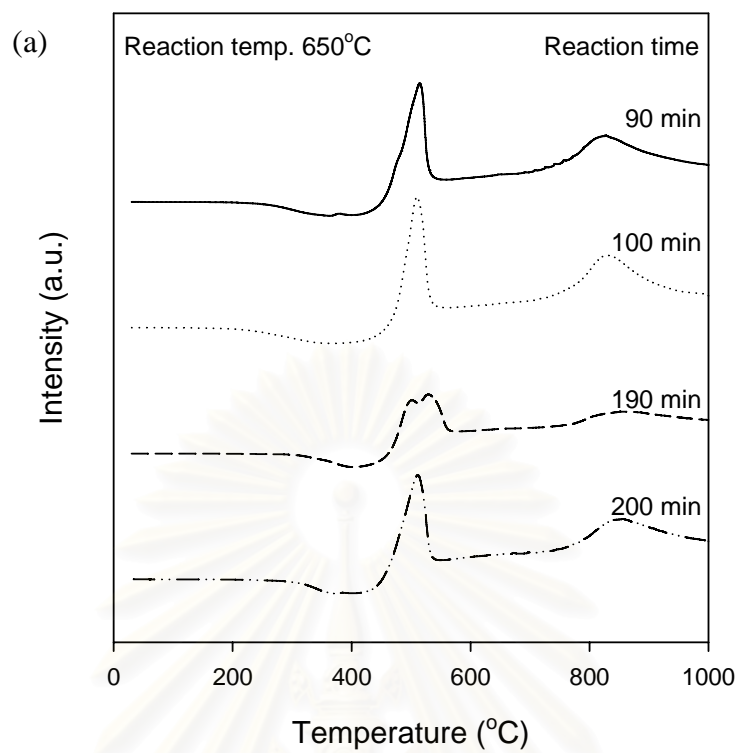


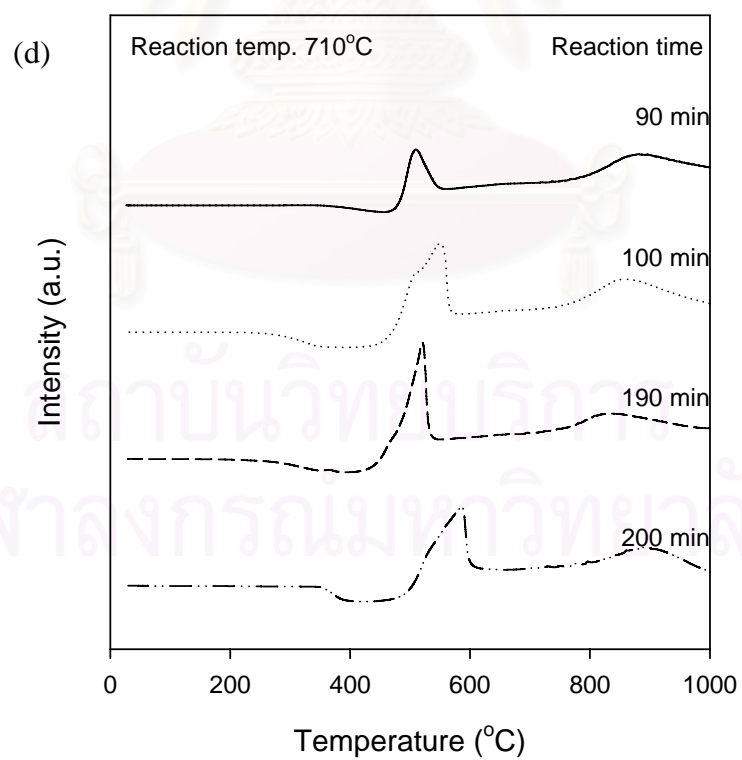
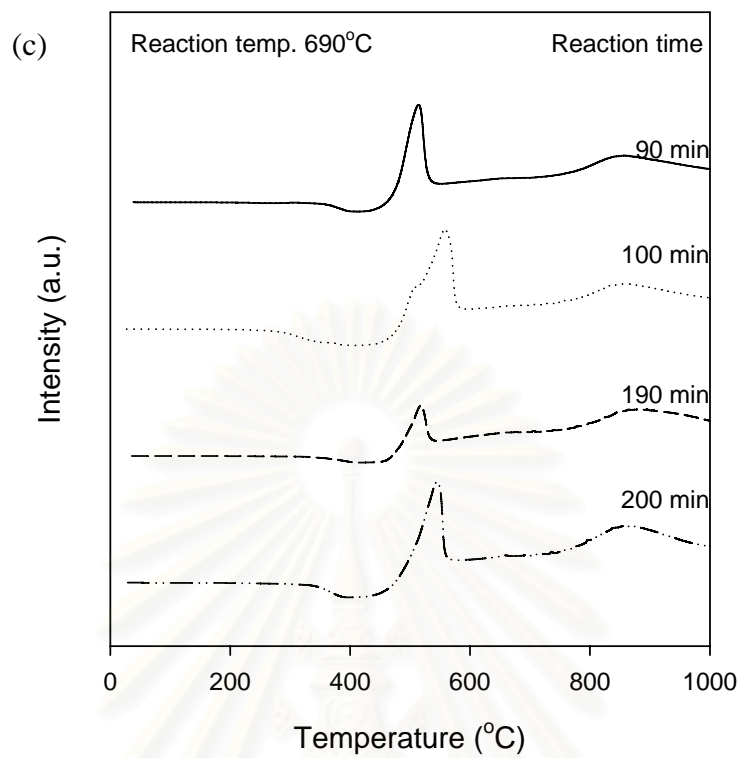
Figure 5.14 XRD patterns of used catalysts at different reaction times and reaction temperatures (a) at 650°C (b) at 670°C (c) at 690°C (d) at 710°C (e) at 730°C (f) at 750°C ▼ Coke ○ Ni ● NiO

Table 5.3 The d-spacing of nickel and coke deposited on catalysts at different conditions

Catalysts	d-spacing of nickel (nm)				d-spacing of coke (nm)			
Fresh	4.83				-			
After reaction at	reaction time							
reaction temp.	90min	100min	190min	200min	90min	100min	190min	200min
650°C	18.23	14.96	14.90	13.86	9.82	10.09	6.50	5.73
670°C	12.97	22.72	14.54	15.45	10.39	29.26	6.34	5.95
690°C	15.60	19.32	15.04	11.16	8.38	17.66	7.03	7.62
710°C	20.80	22.69	25.96	27.61	16.44	33.40	24.52	31.04
730°C	19.53	26.23	29.25	30.69	23.88	37.79	30.03	39.48
750°C	26.88	28.25	27.92	20.90	35.75	39.34	27.36	26.10

TPO profiles of used catalysts at different reaction times and different reaction temperatures are shown in Figure 5.15(a)-(f). The principle of TPO is to evaluate the amount of coke removal off the used catalyst by burning with oxygen flow to form carbon dioxide. According to the result, the profile revealed two peaks of coke at oxidizing temperatures ca. 530 and 880°C. The amount of coke for each peaks were calculated from area beneath curve as shown in Table 5.4. It was found that the behaviors of coke formation for both peaks were different. The amounts of coke for both peaks were also different. The first peak was narrow and high whereas the second peak was board and low. It was found that amount of coke at first peak increased after regeneration with carbon dioxide but that at second peak decreased after regeneration. This indicates that at least 2 different coke were formed on the surface of catalyst. The coke at first peak was probably attributed to coke which was formed via Boudouard reaction ($2\text{CO} \rightarrow \text{CO}_2 + \text{C}$) during regeneration period whereas the coke at second peak was possibly attributed to coke which was formed via methane cracking reaction ($\text{CH}_4 \rightarrow 2\text{H}_2 + \text{C}$). It was also found that at low temperature, the amounts of coke for both peaks were almost not changed with reaction time. In contrast, at high temperature, the amounts of coke were varied with reaction time. This result might influence to the stability of the catalyst for high temperature.





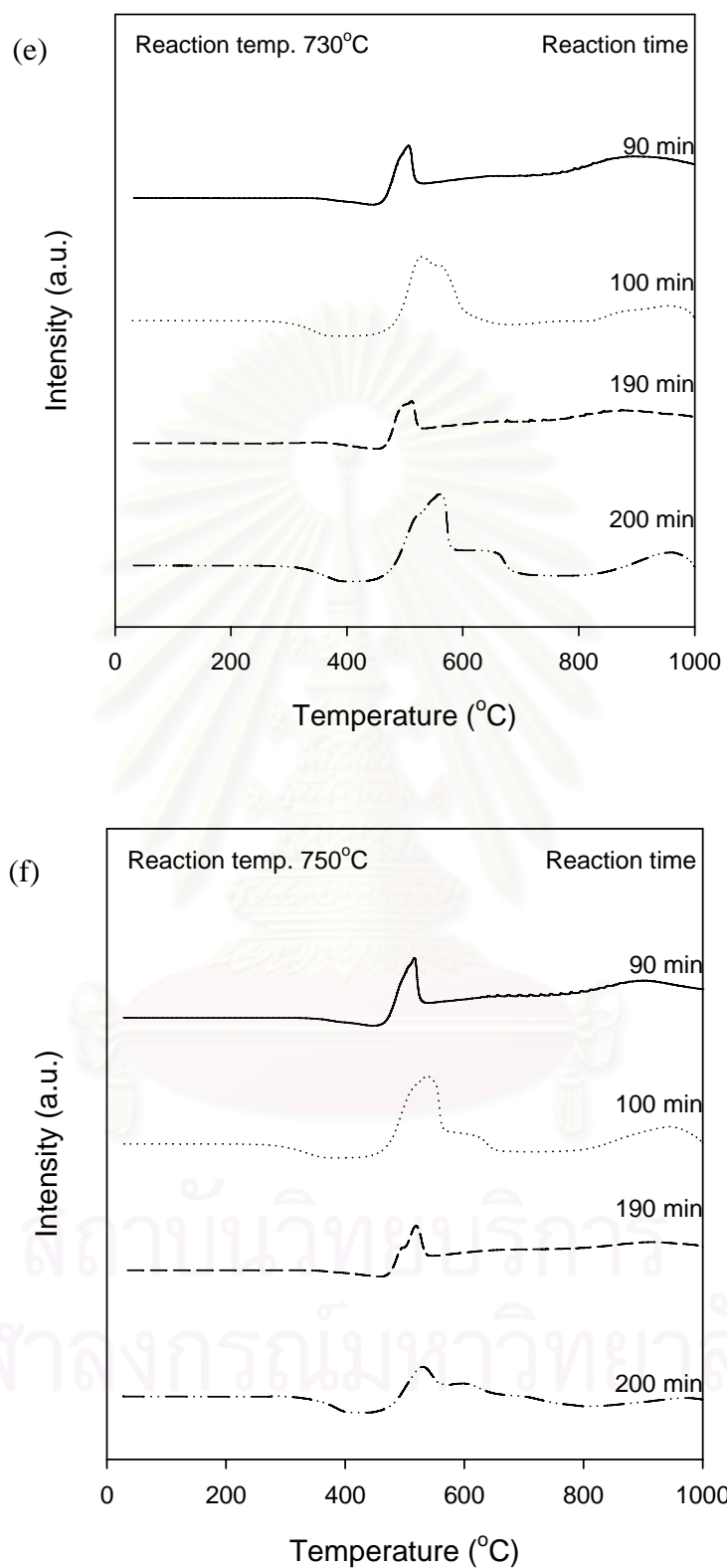


Figure 5.15 TPO profiles of used catalysts at different reaction times and reaction temperatures (a) at 650°C (b) at 670°C (c) at 690°C (d) at 710°C (e) at 730°C (f) at 750°C

Table 5.4 Coke amount obtained from TPO profiles of used catalysts at various reaction temperatures and reaction times

Catalyst		Coke amount (mg)			
Reaction temp. (°C)	Reaction time (min)	Peak 1		Peak 2	
		Temp. (°C)	Amount	Temp. (°C)	Amount
650	90	514.7	5.38	827.2	18.99
	100	510.1	5.30	829.1	18.27
	190	529.3	3.88	851.4	16.73
	200	511.5	4.81	855.9	17.84
670	90	522.5	5.97	836.2	17.45
	100	529.4	4.41	861.3	15.14
	190	489.1	2.88	832.4	15.68
	200	568.1	7.67	845.5	18.48
690	90	514.4	3.75	857.5	15.66
	100	558.2	5.74	860.4	13.82
	190	517.8	1.82	880.2	15.32
	200	544.8	4.66	856.6	17.19
710	90	509.8	2.69	880.4	15.24
	100	550.0	5.58	867.1	14.45
	190	520.7	4.42	834.2	15.36
	200	585.7	4.64	883.8	9.59
730	90	506.4	1.93	892.8	14.88
	100	529.4	5.30	958.1	3.98
	190	511.7	1.70	873.9	12.26
	200	559.9	6.60	960.4	2.74
750	90	516.2	2.04	904.9	13.03
	100	538.5	5.30	945.5	3.63
	190	518.6	1.60	919.2	10.54
	200	530.4	3.14	972.8	1.20

Furthermore, it was also noticed that oxidizing temperature increased with increasing reaction temperature. This result might be due to the increasing size of particle at high temperature. Thus, the oxidation of coke occurred more difficultly.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

In this chapter, section 6.1 provides the conclusions obtained from the experimental results of the reforming activity and the degree of coke deposited on Ni/SiO₂.MgO catalyst from carbon dioxide reforming of methane under both periodic and steady state operations. Additionally, recommendations for further study are given in section 6.2.

6.1 Conclusions

1. By comparing periodic operation with steady state operation for carbon dioxide reforming of methane at range of reaction temperature 650-750°C, it was found that Ni/SiO₂.MgO catalyst showed good stability under steady state operation. Unlikely, under periodic operation, the catalyst showed stability only at low temperature but showed declined activity over reaction time at high temperature.

2. Carbon formation in carbon dioxide reforming of methane under periodic operation presented at least two different cokes taking place on the surface of catalyst at the reaction temperature range 650-750°C. At low temperature, coke was formed in a great amount in the methane cracking period but was incompletely removed in the regeneration period. At this temperature, coke was mostly formed in the structure of filamentous carbon. In contrast, at high temperature, a lesser amount of coke was obtained but it was formed in encapsulating form. Thus, it affected the activity of catalyst.

3. The results of sintering of catalyst and coke deposition affected surface area of spent catalyst. At low temperature, coke deposition played a role to increase surface area due to filamentous carbon forming. At higher temperature, the effect of sintering of catalyst induced size of particle to be larger and lessened surface area.

This caused the blockage of active site of catalyst and brought to the loss of stability of catalyst.

6.2 Recommendations

1. Since the periodic operation of carbon dioxide reforming of methane provides lower activity than the steady state operation and no stability at high temperature. Using the same reaction temperature both cracking and regeneration periods may be not reasonable. Suitable temperature and time for each period should be studied.

2. The combination of carbon dioxide and oxygen is recommended to use in order to enhance the removal of coke from surface of catalyst.

3. To further explain the behavior of catalyst after reaction, the other analytical methods such as active site measurement and mapping study of catalyst content should be investigated.

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APPENDICES

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APPENDIX A

CALCULATION FOR CATALYST PERFORMANCE

The catalyst performance for the carbon dioxide reforming of methane in both periodic and steady state operations was evaluated in many ways.

Periodic operation

Conversion of methane and carbon dioxide

In case of periodic operation, the main reaction in the reactor could be separated to catalytic cracking of methane ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) and catalyst regeneration with carbon dioxide ($\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$). A mixture of reactant and product gas from cracking period (CH_4, H_2) and regeneration period (CO_2, CO) would be collected with the same sampling bag after finished each cycle.

The sample would be taken for analyzing of gas composition from sampling bag. The conversion of methane in cracking period and conversion of carbon dioxide in regeneration period for periodic mode could be gained as followed;

$$\text{CH}_4 \text{ Conversion (\%)} = 100 \times \frac{\frac{\text{mole of H}_2 \text{ outlet}}{\text{mole of CH}_4 \text{ outlet}}}{2 + \frac{\text{mole of H}_2 \text{ outlet}}{\text{mole of CH}_4 \text{ outlet}}} \quad (\text{A.1})$$

$$\text{CO}_2 \text{ Conversion (\%)} = 100 \times \frac{\frac{\text{mole of CO outlet}}{\text{mole of CO}_2 \text{ outlet}}}{2 + \frac{\text{mole of CO outlet}}{\text{mole of CO}_2 \text{ outlet}}} \quad (\text{A.2})$$

Hydrogen yield

Hydrogen selectivity of product gas is also used to compare the performance of steady state with periodic operation. Because of only cracking reaction was conducted for periodic operation to generate hydrogen product, selectivity of H₂ was considered to be 100%. Thus, hydrogen yield for periodic operation equals to the methane conversion.

Steady operation

Conversion of methane and carbon dioxide

Activity of the catalyst performed in term of methane conversion. In case of steady state reaction, methane conversion was defined as mole flow rate of methane reacted during the reaction period ($F_{\text{CH}_4,\text{reacted}}$), with respect to inlet mole flow rate of methane in feed passed through reactor during the reaction period ($F_{\text{CH}_4,\text{in}}$)

$$\begin{aligned}
 \text{CH}_4 \text{ Conversion (\%)} &= 100 \times \frac{F_{\text{CH}_4,\text{reacted}}}{F_{\text{CH}_4,\text{in}}} \\
 &= 100 \times \frac{F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}}{F_{\text{CH}_4,\text{in}}} \\
 &= 100 \times \frac{C_{\text{CH}_4,\text{in}} v_{\text{in}} - C_{\text{CH}_4,\text{out}} v_{\text{out}}}{C_{\text{CH}_4,\text{in}} v_{\text{in}}} \quad (\text{A.3})
 \end{aligned}$$

where $C_{\text{CH}_4,\text{in}}$ = concentration of methane inlet (mol/mL)

$C_{\text{CH}_4,\text{out}}$ = concentration of methane outlet (mol/mL)

v_{in} = volumetric flow rate of total flow inlet (mL/min)

v_{out} = volumetric flow rate of total product output (mL/min)

In this case, volumetric flow rate of total flow inlet (v_{in}) was controlled to be 12.5 mL/min. Volumetric flow rate of total product output (v_{out}) can be calculated from overall flow rate of gas outlet measured from bubble flow meter. Concentration of methane outlet can be calculated from mole of methane in 1 mL injected into GC.

Conversion of carbon dioxide and hydrogen yield also could be obtained in a similar way as calculation of methane conversion.

$$\text{CO}_2 \text{ Conversion (\%)} = 100 \times \frac{C_{\text{CO}_2, \text{in}} v_{\text{in}} - C_{\text{CO}_2, \text{out}} v_{\text{out}}}{C_{\text{CO}_2, \text{in}} v_{\text{in}}} \quad (\text{A.4})$$

Hydrogen yield

Hydrogen yield is calculated from molar flow rate of hydrogen product respect to molar flow rate of methane inlet.

$$\text{H}_2 \text{ Yield (\%)} = 100 \times \frac{C_{\text{H}_2, \text{out}} v_{\text{out}}}{C_{\text{CH}_4, \text{in}} v_{\text{in}}} \quad (\text{A.5})$$

Composition each gaseous product in total gas product (which could be consisted of CH_4 , CO_2 , H_2 , and CO) could be calculated with the calibration curve from Figure B.1-B.4, Appendix B.

$$\text{mole of CH}_4 = (\text{Area of CH}_4 \text{ from integrator plot on GC-8A}) \times (2 \times 10^{-11})$$

$$\text{mole of CO}_2 = (\text{Area of CO}_2 \text{ from integrator plot on GC-8A}) \times (6 \times 10^{-11})$$

$$\text{mole of H}_2 = (\text{Area of H}_2 \text{ from integrator plot on GC-8A}) \times (5 \times 10^{-12})$$

$$\text{mole of CO} = (\text{Area of CO from integrator plot on GC-8A}) \times (5 \times 10^{-11})$$

APPENDIX B

CALIBRATION CURVES

This appendix shows the calibration curves for calculation of composition of reactant and products in the carbon dioxide reforming of methane reaction. The reactants are carbon dioxide and methane. The products are synthesis gas, containing carbon monoxide and hydrogen.

The Gas chromatography Shimadzu model 8A with a thermal conductivity detector (TCD), was used for analyzing the concentration of all reactants and products by using Molecular sieve 5A column and Porapak-Q column, respectively. Conditions used in for GC analyzing are illustrated in Table B.1.

Mole of reagent in y-axis and area reported by gas chromatography in x-axis are exhibited in the curves. The calibration curves of carbon monoxide, carbon dioxide, methane, and hydrogen are shown in the following figures.

Table B.1 Conditions used in Shimadzu model GC-8A

Parameters	Condition (Shimadzu GC-8A)
Width	5
Slope	50
Drift	0
Min. area	10
T.DBL	0
Stop time	30
Atten	5
Speed	2
Method	41
Format	1
SPL.WT	100
IS.WT	1

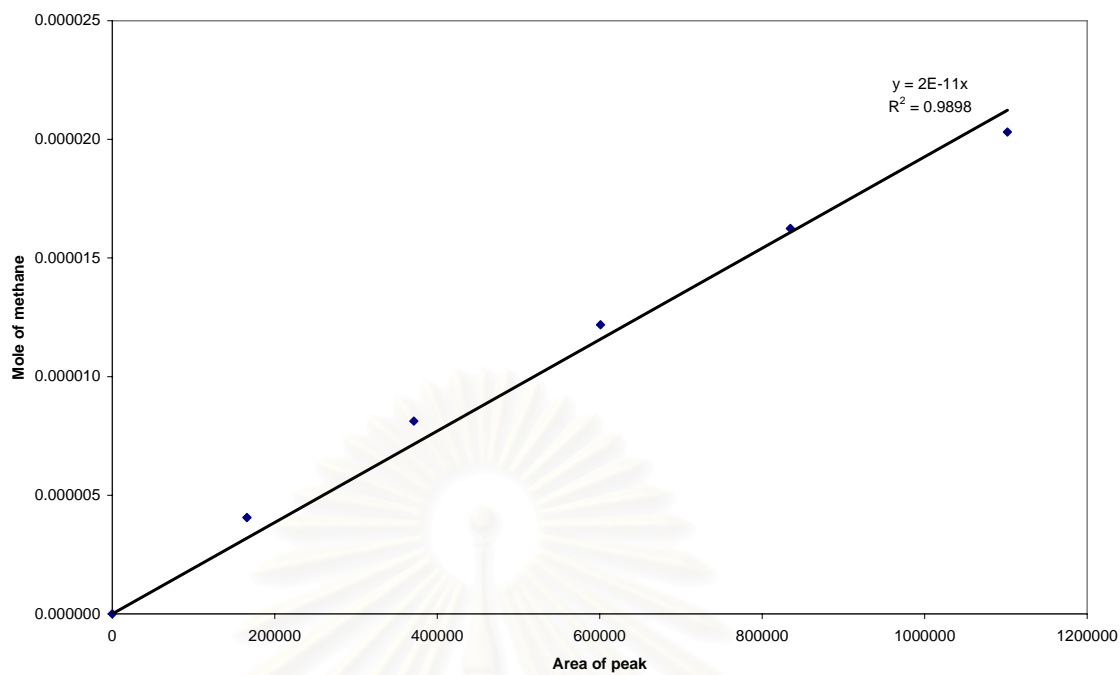


Figure B.1 The calibration curve of methane

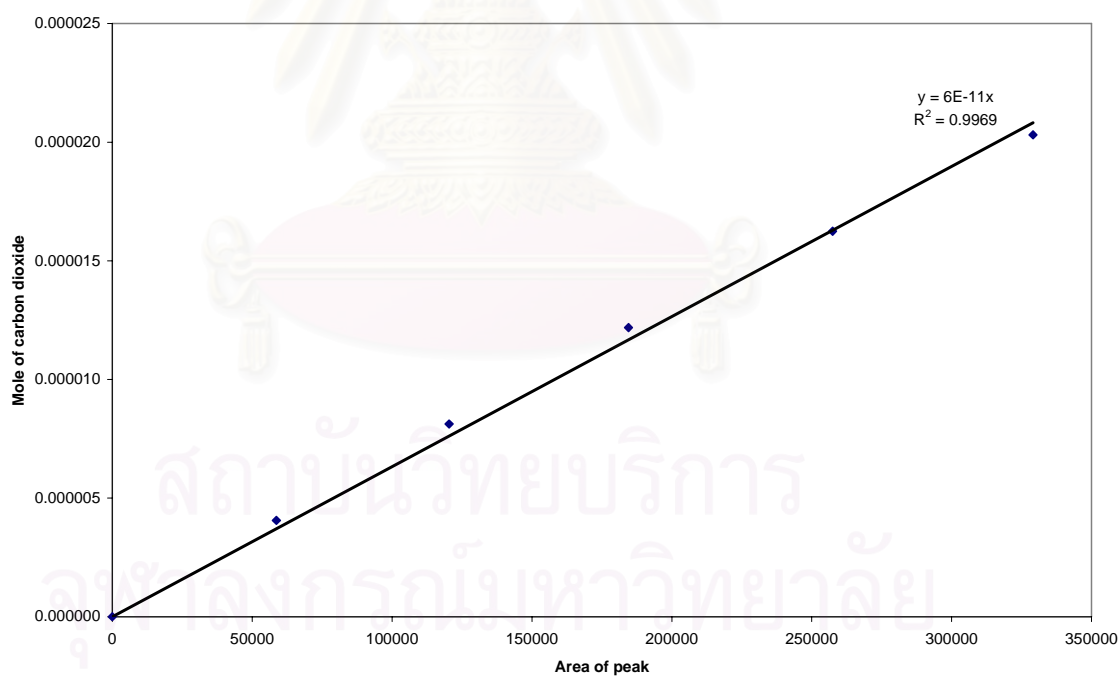


Figure B.2 The calibration curve of carbon dioxide

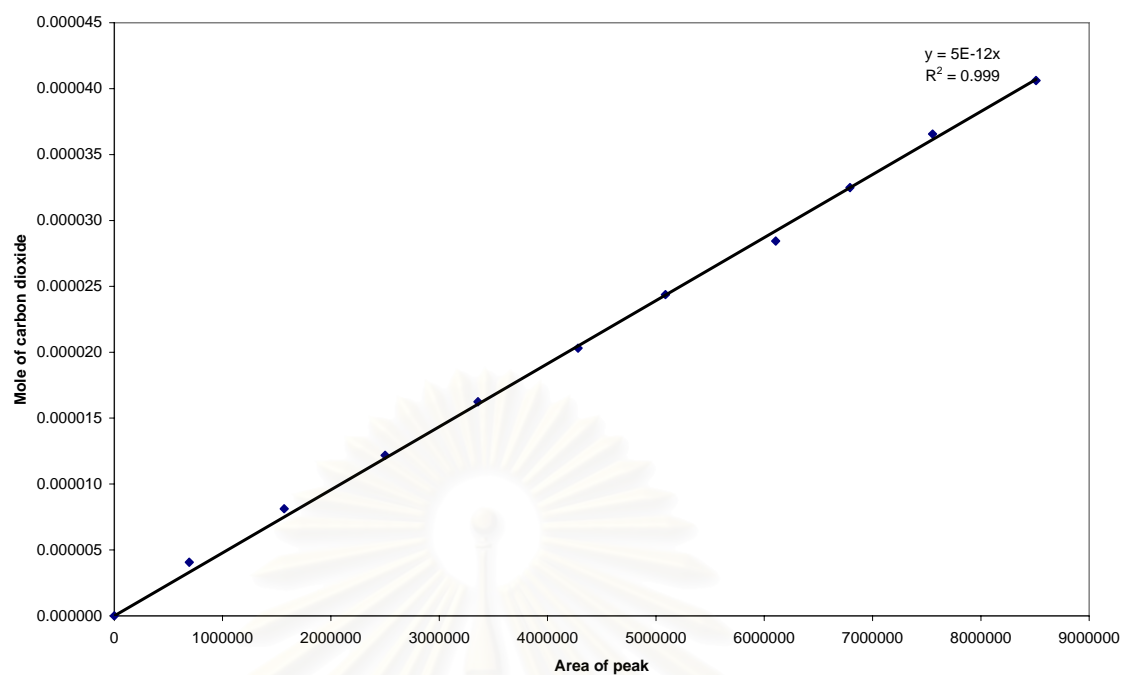


Figure B.3 The calibration curve of hydrogen

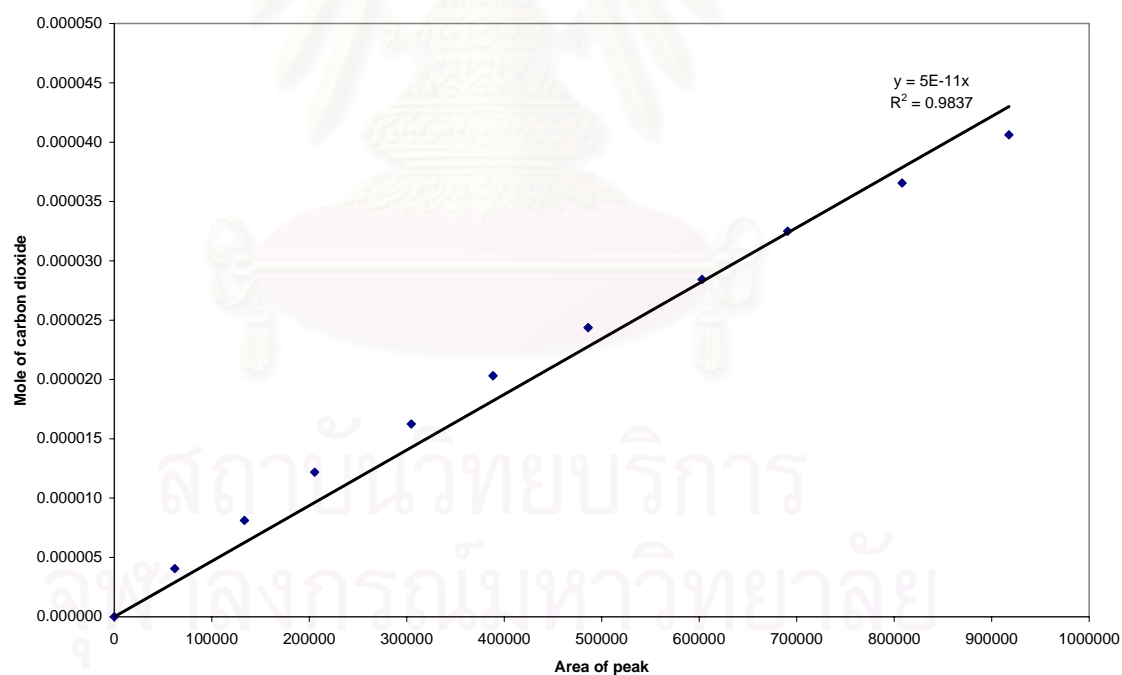


Figure B.4 The calibration curve of carbon monoxide

APPENDIX C

CALCULATION OF THE CRYSTALLITE SIZE

Calculation of the crystallite size by Scherrer equation

The crystallite size was calculated from the half-height width of the diffraction peak of XRD pattern using the Debye-Scherrer equation.

From Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (\text{C.1})$$

where D = Crystallite size, Å
 K = Crystallite-shape factor = 0.9
 λ = X-ray wavelength, 1.5418 Å for CuK α
 θ = Observed peak angle, degree
 β = X-ray diffraction broadening, radian

The X-ray diffraction broadening (β) is the pure width of a powder diffraction free of all broadening due to the experimental equipment. Standard α -alumina is used to observe the instrumental broadening since its crystallite size is larger than 2000 Å. The X-ray diffraction broadening (β) can be obtained by using Warren's formula.

From Warren's formula:

$$\beta^2 = B_M^2 - B_S^2 \quad (\text{C.2})$$

$$\beta = \sqrt{B_M^2 - B_S^2}$$

Where B_M = The measured peak width in radians at half peak height.
 B_S = The corresponding width of a standard material.

Example: Calculation of the crystallite size of Ni obtained by spent catalyst after carbon dioxide reforming of methane reaction under periodic operation at reaction temperature 750°C and reaction time 190 min (PO750C190)

$$\begin{aligned} \text{The half-height width of peak} &= 0.36^\circ \text{ (from Figure C.1)} \\ &= (2\pi \times 0.36)/360 \\ &= 0.00628 \text{ radian} \end{aligned}$$

$$\text{The corresponding half-height width of peak of } \alpha\text{-alumina} = 0.0038 \text{ radian}$$

$$\begin{aligned} \text{The pure width} &= \sqrt{B_M^2 - B_S^2} \\ &= \sqrt{0.00628^2 - 0.0038^2} \\ &= 0.00515 \text{ radian} \end{aligned}$$

$$\beta = 0.00515 \text{ radian}$$

$$2\theta = 26.52^\circ$$

$$\theta = 13.26^\circ$$

$$\lambda = 1.5418 \text{ \AA}$$

$$\begin{aligned} \text{The crystallite size} &= \frac{0.9 \times 1.5418}{0.00515 \cos 13.26} \\ &= 273.64 \text{ \AA} \\ &= 27.3 \text{ nm} \end{aligned}$$

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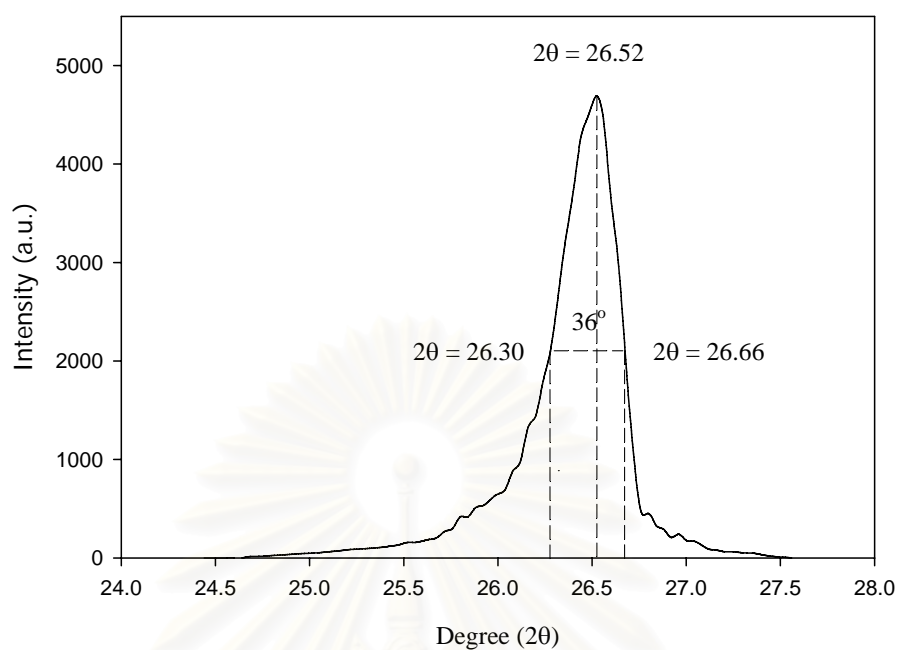


Figure C.1 The measured peak of Ni obtained by spent catalyst (PO750C190) to calculate the crystallite size.

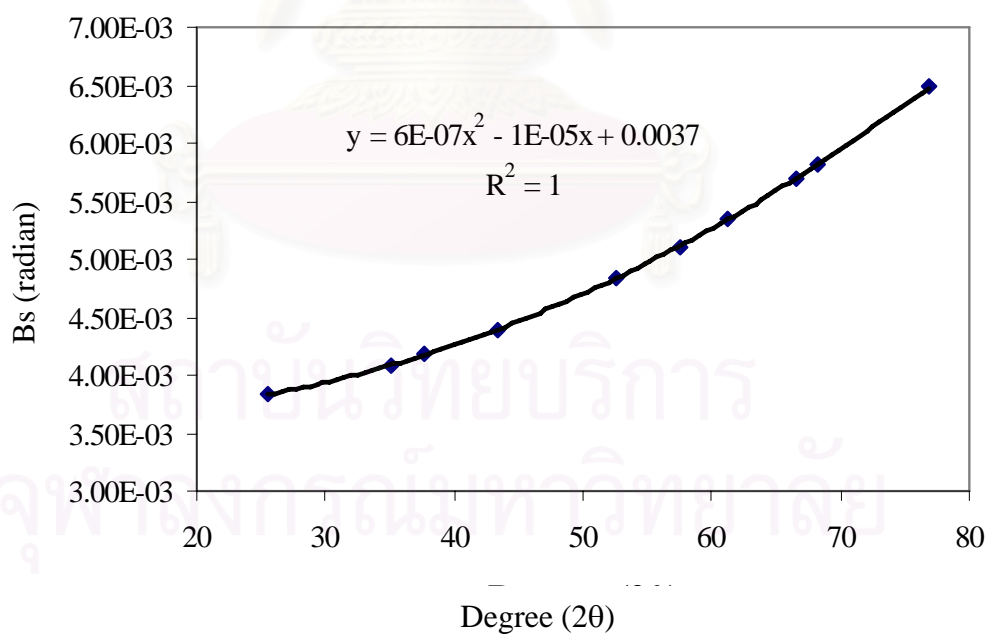


Figure C.2 The plot indicating the value of line broadening due to the equipment. The data were obtained by using α -alumina as standard

VITA

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