ABSTRACT

Carbon dioxide reforming of methane, or dry reforming, is one of the alternative ways to produce synthesis gas. This reaction has many advantages over steam reforming. However, this reaction has an important problem that is carbon deposition on the catalysts. Much effort has been directed toward development of catalysts, which give high activity and stability. The purpose of this work is to study the effect of metal loading, adding promoters, and reaction temperature of carbon dioxide reforming of methane reaction over Ni supported on clinoptilolite, which is the most abundant natural zeolite. The promoter that was selected to be used is Ce. All of the catalysts were prepared by using incipient wetness impregnation method. The reaction was performed at 700°C. The results shown that at 700°C, 8wt%Ni/clinoptilolite gave the highest activity over 1wt%, 3wt%, 5wt%, 10wt%, and 15wt% Ni loading. It gave more than 60% conversion of CH4 and CO2 and also gave high hydrogen selectivity. After added promoters to 8wt%Ni/clinoptilolite, it was found that Ce could enhance both activity and stability of this catalyst. With 3wt%Zr the catalyst gave about 70% conversion of CH4 and CO2.

KEYWORDS
Carbon dioxide reforming of methane, clinoptilolite, Ni based catalysts, Ceria

INTRODUCTION

Carbon dioxide reforming of methane or dry reforming to produce synthesis gas has recently attached much attention. This reaction has important advantages over steam reforming process such as (a) both CH4 and CO2 are the greenhouse gases (b) it can produce low H2/CO ratio, which is suitable for using as the feedstock in Fischer-Tropsch process to synthesis liquid fuel (c) it can be used as chemical energy transmission systems and energy storage in the form of CO and H2 (Wang and Lu, 1996). However, one of the major problems of using this reaction is the catalyst deactivation by carbon deposition. Therefore, it is desired to develop the catalyst, which can stabilize under the operating condition of this reaction.

Numerous supported metal catalysts have been studied for methane reforming. Group VIII metals (Rh, Ru, Ni, Pt, Pd, Ir, Co, Fe) are good for this reforming reaction. Noble metals (Rh, Ru, Pt) are not deactivated by carbon deposition whereas Co, Ni, and Pd are deactivated by coking (Cheng et al., 1996). Richardson et al. (1990) also studied catalysts based on Ni, Ru, Rh, Pd, Pt, and Ir. The deactivation test showed that the Rh catalyst was more stable than the other catalysts. Although the noble metals present high performance, but the limited availability and expensive price lead to the investigation of non-noble metal supported catalyst in order to obtain high catalytic activity and stability for carbon dioxide reforming of methane reaction.

In this work, clinoptilolite was selected to use as the catalysts support due to its micropore structure and high thermal stability that could give promotion effect to the activity of the catalysts. Clinoptilolite is the natural zeolite with the simplified formula (Na,K)6Si30Al6O72·nH2O. It is one of the most abundant zeolites, which can be found in sedimentary rocks all over the world and can be minded.
with simple techniques. It has monoclinic framework consisting of ten-membered-ring (7.5 × 3.1 Å) and two eight-membered-ring (4.6 × 3.6 Å, 4.7 × 2.8 Å) (Lee et al., 2002). It is defined as the heulandite family with Si/Al ≥ 4. The negative charge in the zeolite lattice is typically balanced by Na⁺, K⁺, and Ca⁺ in nature, which make it has high affinity to exchange with metal cations. In carbon dioxide reforming of methane, it has been reported that using zeolite supports are superior to amorphous supports (Chang et al., 1996 and Bhat and Sachtler, 1997). Chang et al. (1996) reported that zeolite-supported Ni catalysts show high performance and little coke formation. Bhat and Sachtler (1997) found that Rh supported on zeolite gave high stability along the reaction, while Rh supported on amorphous oxides supports showed the decreased in activity with time on stream. Therefore, it seems to be interesting to investigate the catalytic possibility of clinoptilolite, the natural zeolite, in carbon dioxide reforming of methane reaction since it has high affinity for carbon dioxide. Moreover, the balanced charges in clinoptilolite e.g. Na⁺, K⁺, Ca⁺ are expected to promote the activity of the catalysts.

MATERIALS AND METHODS

Materials

Nickel (II) nitrate hexahydrate, Ni(NO₃)₂·6H₂O of 98% purity obtained from Fluka Co., Ltd. was used as the Nickel precursor. Clinoptilolite was obtained from Marineland, Moorpark, CA. Promoters precursor which is Cerium (III) nitrate hexahydrate, Ce(NO₃)₃·6H₂O of 99% purity was obtained from Aldrich Chemical Co., Ltd. All of gases in this work were obtained from Thai Industrial Gas Public Co., Ltd.

Catalyst Preparation

A series of Ni/Clinoptilolite catalysts were prepared by using incipient wetness impregnation technique. Supported Ni catalysts with various Ni loading were prepared by impregnating appropriate amount of Ni(NO₃)₂·6H₂O on to supports followed by drying at 110°C and calcining at 500°C for 5 h in air. For the catalysts modified with Ce, the aqueous solution of Ce(NO₃)₃·6H₂O was added to clinoptilolite first. After that the modified support was impregnated by aqueous solution of Ni(NO₃)₂·6H₂O. The impregnated catalysts were dried at 110°C overnight and then calcined in air at 500°C for 5 h.

Catalyst Characterization

Structural characterization of catalysts was investigated by X-ray Diffraction technique to analyze the fresh and spent catalysts qualitatively and quantitatively. Amount and oxidized temperature of carbon deposition on catalysts were estimated by Thermogravimetric Analyzer (TGA). The weight loss from the combustion of the deposited carbon was observed under air flowing by using the Du Pont TGA 2950 Thermogravimetric Analyzer. The temperature was increased from 30 to 800°C with heating rate of 10°C/min. Temperature Programmed Oxidation (TPO) was performed for studying the reactivity of carbon deposits by oxidizing sample under the flow of air while the temperature increases linearly with time. Temperature-programmed reduction (TPR) was performed for monitoring the reduction of the metal oxide while the temperature increased from 60 to 900°C with heating rate of 10°C/min. H₂ pulse chemisorption was carried out at 50°C using H₂ 99.99% purity and repeated at 5 min intervals for 10 times by using Temperature Programmed Desorption Reduction Oxidation (TPDRO/MS 1100). The Ni
dispersion was calculated by assuming the adsorption stoichiometry of one hydrogen atom per nickel surface atom (H/Ni = 1).

**Experimental Procedure**

The catalytic reaction was carried out under atmospheric pressure. Typically, 0.2 g of catalyst was used in each run. Reactant gas was composed of CH₄:CO₂ = 1:1. Prior to each catalytic measurement, the catalyst was reduced in a pure H₂ flow of 30 ml/min at 500°C for one hour, followed by an increase to reaction temperature in He with the flow rate of 40 ml/min. The reactant mixture was balanced by using He with a total flow rate of 100 ml/min for all of the experiments. Using a by-pass line to a GC, the concentrations of the reactant gases were analyzed.

**RESULTS AND DISCUSSION**

**Effect of Ni loading**

A series of Ni/Clinoptilolite catalysts with various amount of Ni loading, 1, 3, 5, 8, 10, and 15wt% were tested for their activity at 700°C. The H₂ pulse chemisorption result showed that the Ni dispersion tends to decrease with the amount of Ni loading after reduced at 600°C for one hour. This can be concluded that higher amount of Ni loading resulted in higher metal sintering as shown in Table 1. Figure 1 shows the XRD results, it is found that the metallic Ni peaks (2θ = 44.5° and 52°) of lower metal loading catalysts are weaker and broader than the catalysts with higher metal loading. This can be suggested that the Ni crystallite size on lower Ni loading catalysts is smaller than on the catalysts with high Ni content. Larger Ni crystallite size resulting in lower Ni dispersion, which is in good agreement with the results of H₂ pulse chemisorption.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Dispersion (%)</th>
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<tbody>
<tr>
<td>5%Ni/clino</td>
<td>1.95</td>
</tr>
<tr>
<td>8%Ni/clino</td>
<td>1.02</td>
</tr>
<tr>
<td>10%Ni/clino</td>
<td>0.30</td>
</tr>
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Figures 2a and 2b show the CH₄ and CO₂ conversion with time on stream of the catalysts with different amounts of Ni. It is clearly seen that the CH₄ conversion increases with increasing amounts of Ni loading from 1 to 8wt%. The 5%Ni/clino gives more than 70% CH₄ conversion initially, which is the highest among the others. But the activity is rapidly decreased with time on stream. The 8%Ni/Clino gives almost the same CH₄ conversion as 5%Ni/clino in the first hour of reaction, but it shows much higher catalyst stability after 5 h. However, the gradual decrease in activity is still observed. When increasing Ni loading to more than 8%, the catalytic activity is decreased to 35% CH₄ conversion. It seems that too high amount of Ni leads to the decrease in the catalytic activity of the catalysts, which might be the results of a large amount of coke, lower Ni dispersion and larger Ni ensemble size that make the catalysts lost their active surface area for CH₄ decomposition (Noronha et al., 2001). In Figure 2b, it is found that the results give the same trend as CH₄ conversion, which 8%Ni/clino shows the best in conversion and stability.
The result of H\textsubscript{2} selectivity and H\textsubscript{2} yield of the catalysts are shown in Figures 2c and 2d, respectively. The results show that the H\textsubscript{2} selectivity increases when increasing the amount of Ni loaded on the catalysts from 3 to 8wt% and when the Ni loading is more than 8wt%, the H\textsubscript{2} selectivity decreases, which is due to lower Ni dispersion. It is found that the H\textsubscript{2} selectivity of these catalysts occurs below 50% which can be suggested that H\textsubscript{2} was consumed in the reverse water gas shift reaction to produce H\textsubscript{2}O. The H\textsubscript{2} yield is used to compare the catalytic activity and stability of the catalysts. The catalyst which gives the highest H\textsubscript{2} yield will be selected to use in the next part to study the effect of promoter. Among five catalysts examined, 8%Ni/clino shows the best activity along 5 h of reaction. It gives H\textsubscript{2} yield about 34% at the initial but decreases with time on stream to 22% in 5 h of reaction because of the deactivation of the catalyst. Therefore, the appropriate amount of Ni loading on clinoptilolite which is selected to use in the next part is 8wt%.

![Figure 2](image1.png)

**Figure 2** (a) CH\textsubscript{4} conversion (b) CO\textsubscript{2} conversion (c) H\textsubscript{2} selectivity (d) H\textsubscript{2} yield of the catalysts with various amounts of Ni loading

**Effect of Promoter loading**

The TPR profiles of the Ce-promoted catalysts are shown in Figure 3a. The profile of unpromoted catalyst shows a reduction peak between 408 and 600\textdegree C and small shoulder at 680\textdegree C. The area under the peak is assigned to the H\textsubscript{2} consumption for reducing NiO to metallic Ni, which is the active site for carbon dioxide reforming of methane reaction (Wang and Lu, 1998). The wideness of the peaks is believed to the different interaction of NiO and the support. The lower reduction temperature is attributed to the small interaction of NiO and support, which is attributed to the reduction of large NiO particles. The higher reduction temperature is attributed to the small NiO, which have stronger interaction of support and NiO (Montoya et al., 2000). For the catalysts modified by Ce, the reduction peaks are slightly shifted to lower temperature, and the area under the peak is higher than the unpromoted catalyst. This can be deduced that CeO\textsubscript{2} can enhance the reducibility of the NiO on the catalyst. However, the reduction peak is occurred between 400 and 650\textdegree C, which is broader than the unpromoted one. This can be assumed that the higher reduction temperature is the result of NiO-CeO\textsubscript{2} interaction. This might be due to the results of partial coverage of NiO by CeO\textsubscript{2} and form strong metal-support interaction, which makes the NiO becomes hard to reduce. Moreover, partial coverage of NiO by CeO\textsubscript{x} can prevent the metal sintering.
to form large metal ensembles resulting in the decreasing of the active surface area and therefore, help maintaining the Ni dispersion. XRD patterns of Ce-promoted catalysts after 5 h of reaction are shown in Figure 3b. It is found that the metallic Ni peaks of spent catalysts tends to decrease and broader with increasing amount of Ce added. This can be deduced that the catalysts with higher Ce loading have higher Ni dispersion than the catalysts with lower Ce loading. Therefore, it is clearly seen that the promotion effect of Ce to the Ni dispersion is one of the reasons that explain the improvement of the catalytic activity.

Figure 3 (a) TPR profiles (b) TPO profiles of Ce-promoted catalysts

TPO profiles of the carbon deposition on the Ni/clino, and Ce promoted catalysts after 5 h of reaction are shown in Figure 4a. As can be seen, carbon is oxidized between 300 and 780°C. The 8%Ni/clino shows the peak at 645°C followed by a hump at 690°C. For Ce-promoted catalyst, the TPO profiles show that the oxidizing temperature is centered at about the same temperature. However, it is found that when increasing the amount of Ce, the area under the profiles tend to increase. This can be suggested that the higher Ce content, the higher amount of carbon is deposited. There were many researchers having explained the relationship between the oxidation temperature and the location of the carbon on the catalyst surface. They proposed that the carbon deposited on or near the metal particles was oxidized at lower temperature than the carbon located on the support because the oxidation of carbon can be catalyzed by metal. Therefore, it can be suggested that the two peaks observed from the TPO profiles of 8%Ni/clino are attributed to the carbon at different locations and a small hump at 690°C of the unpromoted catalyst might be the oxidizing temperature of the carbon deposits on the support and hard to reduce at low temperature. The TGA results are shown in Figure 4b. It is found that the amount of carbon deposited on the catalysts tends to increase with the amount of Ce. The 8%Ni-4%Ce/clino presents 10wt% of carbon deposition, which can be suggested that the rate of CH₄ decomposition is higher than CO₂ dissociation that makes carbon start to accumulate on the metal surface and blocks the active site of the catalyst, resulting in rapid deactivation.

Figure 4 (a) TPO profiles (b) Amount of carbon deposited of Ce-promoted catalysts
Figures 5a and 5b show CH$_4$ conversion of Ce-promoted catalysts. It is found that Ce can enhance the catalytic activity of the catalysts. The CH$_4$ conversion increases with the amount of Ce adding to the catalysts from 1 to 3wt%. But when the amount of Ce increases to 4wt%, the catalyst deactivates rapidly even though it initially gives around 80% CH$_4$ conversion. Even though a slight deactivation of 8%Ni-3%Ce/clino has been found, it shows the best catalytic activity compared to the others. The CO$_2$ conversion of Ce-promoted catalysts is shown in Figure 5b. The results show that the 8%Ni-3%Ce/clino gives the highest CO$_2$ conversion along 5 h of reaction, but the CO$_2$ conversion still decreases with time on stream. Figure 5c shows the H$_2$ selectivity of Ce-promoted catalysts. The results show that the H$_2$ selectivity is increased with the amount of Ce added to the catalyst, which could be attributed to the higher dispersion of metal active sites for methane decomposition to produce H$_2$. However, 8%Ni-4%Ce/clino gives the H$_2$ selectivity more than 50% in the first hour of reaction. But the selectivity is drastically decreased along the reaction. This might be due to the rate of carbon deposition is higher than the rate of carbon removal that makes the catalyst lost its active sites and decreases in catalytic activity, which gives good agreement with the TGA results. Figure 5d shows the H$_2$ yield of the Ce-promoted catalysts. It was found that 8%Ni-3%Ce/clino gave the highest H$_2$ yield as compared to the other amounts of Ce.

**CONCLUSIONS**

In this work, the effects of Ni loading and the addition of promoter have been employed. The main conclusions of this work are as follows:

8wt% is the appropriate amount of Ni loading on the catalysts. Too high amount of Ni content leads to the increase of the ability of Ni sintering and results in low active surface area for the reaction. Moreover, large metal crystallite size can cause rapid deactivation of the catalysts by decreasing the metal-support interfacial area, which is responsible for cleaning the carbon deposition on the metal surface. Therefore, the catalysts with high metal loading become less active toward this reaction.
The stability of the catalysts can be enhanced by adding the promoters. CeO₂ is known as high oxygen storage capacity and reducible material, which can facilitate carbon removal and clean the metal surface. The other promotion effect of CeO₂ is that it retards the particle growth by partial coverage of CeOₓ species on Ni particle results in strong-metal support interaction, and maintains the expose metal active sites. These are the reasons why Ce can improve catalytic activity and stability of the catalysts.

However, a slightly decrease in the catalytic activity with time on stream was still observed. This can be ascribed to the effect of the unbalancing between the rate of carbon deposition and the rate of carbon removal. Based on two-path mechanism proposed by Stagg and Resasco (1998), if the rate of carbon deposition is higher than the rate of carbon removal, carbon starts to accumulate on the metal surface and cause the catalyst deactivation.

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