

CHAPTER I

INTRODUCTION

Carbon dioxide reforming of methane, also known as dry reforming, has interested the scientific community for a long time. The reaction is particularly interesting because both CH₄ and CO₂ are relatively inexpensive feedstocks due to their natural abundance and the utilization of these two greenhouse gases. Therefore, it is a good alternative to dry reforming, which is mainly used for synthesis gas (CO+H₂) in the industry because it yields lower H₂/CO ratios. Synthetic gas is used for the Fischer-Tropsch synthesis of long-chain hydrocarbons (Bradford, 1999).

Commercially, nickel-based catalysts are used for methane reforming reactions due to it as well as noble metals as relatively cheap and stable, respectively. However, the nickel-based catalyst is suffered from carbon deposition and sintering at elevated reaction temperatures leading to the reduction of activity. This serious problem has led many researchers to study the modification of nickel catalyst in order to increase its stability (Pompeo *et al.*, 2005).

In recent years, many researchers have improved nickel supported on CeO_x-ZrO_x mixed oxides to prevent coke formation and increase activity. It has been reported that the addition of ZrO₂ to ceria (CeO₂) leads to improvements in ceria's oxygen storage capacity, redox properties, thermal resistance and better catalytic activity at lower temperatures. It was also found to be due to the partial substitution of Ce⁴⁺ with Zr⁴⁺ in the lattice of ceria, which results in a solid solution formation (Hori *et al.*, 1998). The mole atom ratio of Ce/Zr affects activity methane oxidation, Ce_{0.75}Zr_{0.25}O₂ reported to exhibit the highest activity for CO oxidation (Thammachart *et al.*, 2001). They found that the catalytic activity and carbon formation for the catalysts studied were significantly dependent on the Ni content and the nature of support. The 15%Ni/Ce_{0.75}Zr_{0.25}O₂ catalyst exhibited the highest catalytic performance in terms of C-C breakage conversion and hydrogen yield (Thaicharoensutcharittham *et al.*, 2011). In addition, the Mn-doped catalysts, Ni/Ce_{0.75}Zr_{0.25-x}Mn_xO₂ (x = 0.10, 0.20, 0.25), possessed much lower amounts of carbon formed as compared to the amounts formed on the Ni/ α -Al₂O₃ and Ni/Ce_{0.75}Zr_{0.25}O₂ catalysts. The incorporation of Mn into Ce_{0.75}Zr_{0.25}O₂ mixed oxide

was able to modify the redox properties of the mixed oxide support (Bampenrat *et al.*, 2010). Adding Mg at low contents resulted in decreasing the catalytic activity but increasing the catalytic stability (Arunsingkaratet *et al.*, 2012). For the effect of Mg incorporating sequence, they found that the Ni-Mg/Ce_{0.75}Zr_{0.25}O₂ possessed higher catalytic activity but lower carbon deposition resistance than the Mg-Ni/Ce_{0.75}Zr_{0.25}O₂. In recently, the Ce_{0.75}Zr_{0.25-x}Mg_{2x}O₂ (x = 0.07-0.21) supports were synthesized by sol-gel method via urea hydrolysis with the Ni loading about 15 wt% (Sukkaao *et al.*, 2013). The results showed that the catalyst was more resistance to carbon deposition and higher catalytic activity than the supports of without Mg. The basicity scale of oxides used in many research groups can be elaborated, according to the CO₂-TPD, as follows: MgO > Al₂O₃ > CeO₂ > TiO₂ > SiO₂. In the case of the acid function multi-component addition affects both the strength and amount of support acid sites. Higher acid strengths increase the acid-catalyzed coking and cracking rates while milder acid strengths benefit isomerization rates due to the inhibition of consecutive cracking and polymerization reactions towards the catalytic performances of several solid acids (Mazzieri *et al.*, 2005). The surface acid-base properties proved to play an important role in the acid-base catalyzed reactions and can be characterized by a large number of techniques, for example, temperature programmed desorption (TPD) of ammonia.

The modifications of the support basic function depend on the amount and acid/base properties of the solid-solution supported. In this study, nickel-based catalysts between Mn and Mg loading on CeO₂-ZrO₂ support have been investigated and compared their performances. The support has been prepared by sol-gel and co-precipitation methods in which mole atom of cerium is fixed at 0.75 while those of zirconium and two metals are compromised. The prepared catalysts will be characterized by means of BET surface area measurements, H₂ temperature programmed reduction (H₂-TPR), temperature programmed oxidation (TPO), temperature programmed desorption (TPD), X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). The catalytic activity and stability to carbon deposition for methane dry reforming will be investigated in the adjusted sequentially temperature range of 500-900 °C in which the temperature interval is 50 °C at atmospheric pressure.