CHAPTER 6
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The chief objectives of the research on synthesized all catalysts and its reforming activity carried out in this dissertation were:

- To synthesize the nano-sized CeO_2 by different microemulsion methods.
- To synthesize the nano-sized CeO_2, CeO_2-ZrO_2, Ni/CeO_2, and Ni/CeO_2-ZrO_2 by colloidal emulsion aphrons (CEAs) method.
- To investigate the effect of cerium source, surfactant type, calcination temperature, and the water content on the CeO_2 powders.
- To investigate the reforming reactivity over all synthesized catalysts.

Overall, the three goals stated above were achieved and systematically categorized into main two parts. Firstly, the three different types of microemulsion (RM, ELM, and CEAs) were used for prepared CeO_2. Then the suitable method of prepared which provided nanometer particle size, high surface area, and high purity was selected. Next, the effect of cerium source, surfactant type, calcination temperature, and the water content on the CeO_2 powders were investigated. Secondly, the CeO_2 obtained from the first part was improved by adding ZrO_2 for higher thermal stability and selected nickel as an active metal loaded on CeO_2 powders for the high activity in reforming process with three different procedures. Then, the suitable procedure of preparation which provided high hydrogen consumption, high surface area, and high methane conversion was selected to prepare Ni on CeO_2-ZrO_2. Next, all the synthesized catalysts have been test for methane steam reforming process.

In the first part (Chapter 4), nano-size CeO_2 was successfully prepared by different types of microemulsion. The results from TEM, BET, and DLS indicated that CeO_2 prepared by CEAs method shows the smallest particle size, the highest surface area, and smallest emulsion droplet, which means this method, is a good and suitable to catalyst preparation. The CeO_2 prepared by CEAs method using $(NH_4)_2Ce(NO_3)_6$ and PE4LE as a cerium source and a surfactant, respectively, shows the smallest particle size and the highest surface area. The surface tensions of cerium solution have slightly effect on the particle size. Cerium compound that has low surface tension, can disperse to small droplets in emulsion easily, as a result, the small particles are produced. To investigate the effect of surfactant type in the case of nonionic on the synthesized CeO_2 found that the hydrocarbon chain length of surfactant have affection of solubility in emulsion and can be decrease particle size. However, compared between nonionic surfactant (PE4LE) and anionic surfactant indicated that the average particle size of CeO_2 obtained from nonionic are bigger than anionic surfactant. This result can be considered as the reason that the stabilizing effect of nonionic surfactant on water droplets and particles mainly derives from its hydrogen bond with water. This action is weaker than that of ion bond. A mutual repulsion between hydrophilic group of the cationic surfactant (CTAB) and nanoparticle surface might be weaker; as a result, CeO_2 particles obtained from cationic became larger than that used nonionic surfactant. The effect of calcination temperature on the particle size of CeO_2 shows that calcinations in higher temperature make the average size of products increasing. By increasing the water content the final particle of CeO_2 was increased because of the size of the final particle much depend on the size of the droplets in the emulsion core which are influenced by the water content.

In the second part (Chapter 5), the CeO_2 was improved by adding ZrO_2 prepared by CEAs method. After drying**,** surface areas of CeO_2 was increased by added CeO_2-ZrO_2. According to the experiment, adding ZrO_2 to CeO_2 provided higher surface area than those from pure CeO_2, which means the increasing of the thermal stability. Moreover, reported that the addition of ZrO_2 to CeO_2 improved the activity of CeO_2, the oxygen storage capacity, redox property, and enhanced the removal activity for CO, NO_x and hydrocarbons under dynamic air-fuel ratio condition. Next, the three different procedures of CEAs were used for prepared Ni/CeO_2. The results indicated that the synthesized procedure of Ni/CeO_2 by impregnated CeO_2 (from the first part) into colloidal emulsion aphrons of nickel solution shows the highest amount of hydrogen uptakes and the highest methane conversion. Therefore, this method was a suitable to catalyst preparation. All the synthesized catalysts have been test for methane steam reforming process. The result shows that, the advantages of using Ni as an active metal on CeO_2 and CeO_2-ZrO_2 based supports are the high reforming reactivity. Therefore, Ni/CeO_2 and Ni/CeO_2-ZrO_2 presented much higher reactivity toward the methane steam reforming than CeO_2 and CeO_2-ZrO_2. It should be noted that the adding of ZrO_2 can stabilize the surface area of CeO_2, which means the increasing of the thermal stability, the oxygen storage capacity, and the redox property. As the reason, the steam reforming reactivity of CeO_2-ZrO_2 was higher than CeO_2. The methane steam reforming activities of Ni/CeO_2-ZrO_2 prepared by CEAs method was highest. In addition, Ni/CeO_2-ZrO_2 prepared by CEAs method shows the carbon formation was lowest, which means that this preparation method is a good reforming catalyst in term of the high resistance toward the carbon formation compared from other method. However, CEAs method have the main advantages to produced the particle with high surface area, the use of high surface area of catalyst significantly reduces the degree of deactivation by thermal sintering compared to general low surface area catalyst.

6.2 Recommendations

The recommendations for further study arising from this work are as follow:

In Chapter 4, the synthesized cerium oxide powder by colloidal emulsion aphrons using only nonionic surfactant (TWEEN80) in the step of colloidal gas aphrons (CGA) preparation. Anionic, cationic, and nonionic surfactant which different hydrocarbon chain length should be used to compared.

In Chapter 5, the advantages of using Ni as an active metal on CeO_2-ZrO_2 based supports are the high reforming reactivity. Therefore, the effect of Ni content on the CeO_2-ZrO_2 catalyst should be investigated in the methane steam reforming process. In this study used only Ni as an active metal, therefore, to compare the active metal on the catalyst performance another active metal such as copper were used.