CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

Rare-earth oxides have been widely investigated as structural and electronic promoters to improve the activity, selectivity and thermal stability of catalyst. The most significant of oxides of rare-earth elements in industrial catalysis is certainly CeO_2. Its use in catalysis has attracted considerable attention in recent years, especially for those applications, such as treatment of emissions, where ceria has shown great potential. This is documented by the increasing number of scientific articles that have appeared on this topic in the last few years.

This review first discusses the method to prepared CeO_2 nanoparticle. As described, CeO_2 has a great potential to be used as the reforming catalyst for the indirect internal reforming solid oxide fuel cells (SOFCs); however, the main weaknesses of CeO_2 are its low specific surface area and high deactivation due to the thermal sintering when operated under SOFC conditions. Therefore, the use of high surface area ceria –based materials as the catalyst support would be a good alternative to improve the steam reforming performance [3]. Some researches improved the thermal stability and redox property by adding ZrO_2 to CeO_2 and improved catalytic activity by doping on CeO_2 surface. Several methods for the preparation of Ni/CeO_2 and Ni/CeO_2-ZrO_2 are reviewed in next part. The stability and the activity of CeO_2, Ni/CeO_2 and Ni/CeO_2-ZrO_2 were then studied and compared in the methane steam reforming is then considered. Finally, the comment on the previous works linking with the goal of the present work is discussed at the end of this chapter.

2.2 Preparation of CeO_2 nanoparticles

This section mentions in the method to prepared CeO_2 in nanoparticles size. Several method are available for the preparation of nano-sized CeO_2, e.g. sol-gel technology, solvothermal and hydrothermal synthesis, precipitation method, machanochemical, surfactant-assisted method, thermal degradation and microemulsion synthesis [4].

Zang *et al.* [5] synthesized CeO_2 crystals by microemulsion technique and they studied changes in crystalline structure at different temperatures. It was found that, heat treatment over 773 K converted Ce^{3+} to Ce^4+ and the cubic crystalline structure characteristic of CeO_2 developed. He *et al*. [6] reported the preparation of monodisperse CeO_2 nanoparticles by homogeneous precipitation using a W/O microemulsion as a microreactor. They studied the stabilizing effect of surfactants. It was described that the particle size and the dispersity increased by increasing calcination temperature. Chen *et al*. [7] synthesized CeO_2 nanoparticles in alcohol/water mixtures, controlling size by varying the alcohol/water ratio and the chemical nature of the alcohol used. They found that the size of the particles decreased with increasing alcohol/water ratio and molecular weight of alcohol. Another method for the preparation of monodisperse CeO_2 is synthesis in polyalcohols, which is affected by pH, temperature, the chemical nature of the polyalcohol and the concentration of the reactants [8]. Zhou *et al*. [9] synthesized spherical ceria crystallites by hydrothermal treatment. It was found that these spheres were developed from gradual aggregation of small nanoparticles and size of the spheres could be tailored by adjusting the reagent concentrations. Another preparation method was described by Phontammachai and co-workers [10], these authors prepared a high surface area ceria by sol-gel process. It was found that the gel can be formed at 0.8–1.1 HCl:alkoxide and 50–65 water:alkoxide molar ratios. Gelation time increases and the specific surface area decreases with increasing amount of HCl. Calcination temperature and time affect the specific surface area and the crystallinity. The highest specific surface area was obtained at 0.8:1:55 HCl:alkoxide:water molar ratio gel calcined at 400°C for 1 h (180 m^2/g). Rebellato *et al.* [11] synthesized CeO_2 particles by precipitation, microemulsion, and marcilly method. They studied the dependence of particle size on the preparation method applied and found that the sample prepared by the marcilly method had the smallest particle size. Bumajdad *et al.* [12] used anionic, cationic and non-ionic surfactants in their syntheses. The largest specific surface area was attained in the experiment using non-ionic surfactant.

2.3 Preparation of Ni/CeO_2 nanoparticles

Very recently, some researches have successfully applied Ni on CeO_2 based support to CO_2 reforming of methane. To achieve higher surface area desirable for better catalytic and redox performance, several efforts have been made to fabricate Ni/CeO_2.

Roh *et al.* [14] prepared nickel oxide dispersed on CeO_2 by co-precipitation method. It was found that the Ni/CeO_2 catalysts showed relatively high activity and stability. The surface area of Ni/CeO_2 was 40 m^2/g. These advantages result in better dispersion of Ni, higher Ni surface area and enhanced oxygen transfer. Another preparation method was described by Srinivas *et al.* [16], these authors prepared NiO-CeO_2-ZrO_2 catalysts of different compositions by hydrothermal process. The hydrothermal synthesis by the rotation method has yielded materials with smaller crystallite size and larger specific surface area (71–107 m^2/g). The Ce/Zr ratio and Ni-content both influenced the crystallite sizes. Laosiripojana and Assabumrungrat [17] prepared Ni/Ce–ZrO_2 by impregnating Ce–ZrO_2 with a $Ni(NO_3)_2$ solution with different Ce/Zr ratio. The results showed that the Ni/Ce–ZrO_2 with Ce/Zr ratio of 3/1 showed the best performance in term of activity and stability. The surface area was 18 m^2/g after running the reaction at 900°C for 10 h.

2.4 Methane steam reforming over CeO_2 and Ni/CeO_2 based catalyst

In recent years, the steam reforming of methane has become an interesting alternative for the production of synthesis gas (H_2 and CO). This reaction produces a $H_2/CO \approx 1$, which is more suitable for obtaining sulfur-free synthetic liquid fuels (by the Fischer–Tropsch reaction) and valuable oxygenated chemicals than the H_2/CO ratio coming from the traditional steam reforming process [18]. In addition, it has been accepted that the catalytic activity depends on the nature of the support, active phase precursor, synthesis method, and pretreatment. Nickel based catalysts have shown an excellent behavior in this reaction, with an activity comparable to noble metal catalysts [17]. Ni has been supported on different materials such as MgO, Al_2O_3, promoted-Al_2O_3, TiO_2, CeO_2, etc. However, most of these tend to deactivate by coke formation, which is closely related to the catalyst structure and composition.

Palikanon *et al.* [19] studied the methane steam reforming over Ni on high surface area CeO_2. Ni/CeO_2 (HSA) presented better resistance toward carbon formation than the general Ni/CeO_2 (LSA), and Ni/Al_2O_3 at the same operating condition. Lee *et al.* [20] studied the methane conversion with different Ni/ZrO_2 anode materials. For 60 vol% Ni cermets, they found activation energy of 98 kJ mol^{-1}. Shan *et al.* [21] had researched on Ni/CeO_2 catalysts in the CH_4 combustion reaction it was found that the highly dispersed

NiO shows good redox property with the adsorbed oxygen and oxygen vacancy, and is the active site for methane combustion. The Ni^{2+} in the solid solution Ni/CeO_2 is difficult to be reduced and shows less activity for methane oxidation.