# 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/$CeO_2$ and Ni/$CeO_2$-$ZrO_2$

Very recently, some researches have successfully applied zirconia support to $CO_2$ reforming of methane. Moreover, they have also successfully applied Ni/$CeO_2$–$ZrO_2$ to partial oxidation of methane reaction [13]. To achieve higher surface area desirable for better catalytic and redox performance, several efforts have been made to fabricate Ni/$CeO_2$ and Ni/$CeO_2$–$ZrO_2$.

Roh *et al.* [14] prepared nickel oxide dispersed on $CeO_2$, $ZrO_2$, and cubic $Ce_{0.8}Zr_{0.2}O_2$ by co-precipitation method. It was found that the Ni/$CeO_2$ and Ni/$CeO_2$–$ZrO_2$ catalysts showed relatively high activity and stability. The surface area of Ni/$CeO_2$, Ni/$ZrO_2$, and Ni/$Ce_{0.8}Zr_{0.2}O_2$ were 40, 54, and 92 $m^2/g$, respectively. The co-precipitated Ni/$Ce_{0.8}Zr_{0.2}O_2$ catalyst has higher BET surface area, smaller nano-crystallite sizes of both $Ce_{0.8}Zr_{0.2}O_2$ support. These advantages result in better dispersion of Ni, higher Ni surface area and enhanced oxygen transfer. $CeO_2$ modified $ZrO_2$ support was prepared by a sol–gel method. The weight ratio of $ZrO_2$:$CeO_2$ was 4:1. The modified support was calcined at 800°C for 6 h. BET analysis showed that the surface area was 55 $m^2/g$ [15]. 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 $CeO_2$, Ni/$CeO_2$ and Ni/$CeO_2$-$ZrO_2$ 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 $CeO_2$ and $CeO_2$-$ZrO_2$ with different the Ce/Zr ratio. The Ce/Zr ratio of 3/1 showed the best performance in terms of activity and stability toward methane steam reforming. Both Ni/$CeO_2$-$ZrO_2$ (HSA) and Ni/$CeO_2$ (HSA) presented better resistance toward carbon formation than the general Ni/$CeO_2$, Ni/$CeO_2$-$ZrO_2$, 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. Ceria-zirconia support ($CeO_2$/$ZrO_2$ wt. ratio, 1:4) was prepared by sol–gel method and loaded Ni (15% wt) on the support by molten-salt method was studied in methane steam reforming process. The catalytic performance of Ni/Ce–$ZrO_2$ is attributed to the combination of several advantages, i.e. high oxygen storage capacity of ceria in Ce–$ZrO_2$ solid solution, strong interaction between Ni and Ce–$ZrO_2$, basic property, and rather high capability for $H_2$ uptake [22].