CHAPTER I

INTRODUCTION

1.1 Significance of Research

Biomass has gained an increasing attention as a potential source of renewable energy. Biomass gasification is one of the most promising conversion routes for producing a fuel gas that can be used for power generation or synthesis gas applications. Gasification involves partial oxidation of raw material to obtain a mixture of hydrogen, carbon monoxide, water, and small amount of methane and higher hydrocarbons.

One of the major problems with gasification is tar which is a complex mixture of aromatics that are produced during the gasification process (Sutton *et al.*, 2001; Devi *et al.*, 2003). Tar is undesirable because of various problems associated with condensation of tar, formation of tar aerosols and polymerization to form complex structures leading to problems in the subsequent process equipments. Moreover, this tar is dangerous since it is carcinogenic and possibly mutagenic substance (Abu El-Rub *et al.*, 2004). Therefore, elimination of tar in flue gas from biomass gasification is necessary to obtain a technically feasible in advanced gasification process.

In general, tar can be removed by physical (e.g. scrubbing and filtration), non catalytic (e.g. thermal cracking), and catalytic tar elimination processes. In physical removal method, tar is not completely eliminated. The technique merely transfers the problem from the gas phase to the condensed phase. Moreover, when tar is removed from the product gas stream, the heating value is decreased. Thermal cracking is an option requiring hot gas conditioning. It requires the exit temperatures higher than those in typical gasifier (> 1,100 °C) in order to achieve high conversion. Moreover, the thermal cracking of tar produces soot that is an unwanted impurity in the product gas stream. Therefore, the catalytic tar elimination is considered as a promising technique to destroy or reform the tar compounds.

To date the majority of catalysts studied for tar elimination are alkali metals, nonmetallic oxides or calcined rocks, and transition metals catalysts. Although alkali

metal-based catalysts are considered as effective catalysts for H_2O and CO_2 gasification of carbon (Suzuki *et al.*, 1992). However, alkali metals are difficult to recover and this is not always cost effective for the gasification process. Among of calcined rocks, dolomite has been proven to be a very effective bed additive in terms of tar reduction. Although dolomite is generally cheap, cannot eliminate tar to the low levels in most gas applications. In addition, dolomite is soft and thus gets eroded by the silica sand particles. Also, some dolomite particles break during the calcination and give rise to a large production of fine particles (Wang *et al.*, 2005). On the other hand, nickel catalyst supported on alumina is cheaper and sufficiently active than other metals such as Pt, Ru, and Rh and seem to be the most widely used commercially (Garcia *et al.*, 2000; Gebhard *et al.*, 1994; Baker *et al.*, 1987), but the major problem with Ni-based catalysts is the fast deactivation due to carbon deposition on the catalyst (Srinakruang *et al.*, 2005; Wang and Lu, 1996; Rostrup-Nielsen, 1983). The use of Ni on different supports such as CaO, SiO_2 and MgO was reported (Au *et al*, 1996; Tang *et al.*, 1998). It was reported that the use of supports in the presence of basic sites such as MgO resulted in enhanced activities and lower carbon deposition (Tang *et al.*, 1998). On the other hand, the use of reducible supports could result in better activity and decrease carbon deposition (Noronha *et al.*, 2001; Pantu *et al.*, 2002).

The use of supports, especially for ceria-based metal oxides, can be depressed the formation of carbon on the nickel surface (Sánchez-Sánchez *et al.*, 2007; Miyazawa *et al.*, 2006). Moreover, it is known that the substitution of Ce^{4+} with Zr^{4+} in the lattice of CeO_2 leads to improvement in its oxygen storage capacity, redox property, and thermal resistance. With the unique properties and high oxygen storage capacity, $Ce_{1-x}Zr_xO_2$ mixed oxides have been utilized for the oxidation of hydrocarbons and the removal of post-combustion pollutants (Thammachart *et al.*, 2001; Pengpanich *et al.*, 2002).

From the above reason, the search for more active and cost-effective catalysts based on metal oxides for the elimination of tar and resistance towards carbon formation remains essential. Therefore, the present proposed research study aims at a better understanding of the activities of $Ce_{1-x}Zr_xO_2$ mixed oxide catalysts toward the tar removal.

1.2 Objective and Outline of Thesis

The main objective of this thesis was to elucidate and develop the catalysts for tar elimination with emphasis on superior resistance to carbon formation in biomass gasification process. The catalysts used in this dissertation were based on CeO_2-ZrO_2-based mixed oxides and Ni supported on CeO_2-ZrO_2-based mixed oxides. Overview of this thesis is given in Figure 1.1.

Investigation of the activities and reaction kinetics of $Ce_{1-x}Zr_xO_2$ mixed oxide catalysts (support)

Comparative investigation of the transition metal oxide-doped CeO_2-ZrO_2 mixed oxide catalysts

Investigation of the transition metal oxide-doped CeO_2-ZrO_2 supported Ni catalysts toward coking resistance
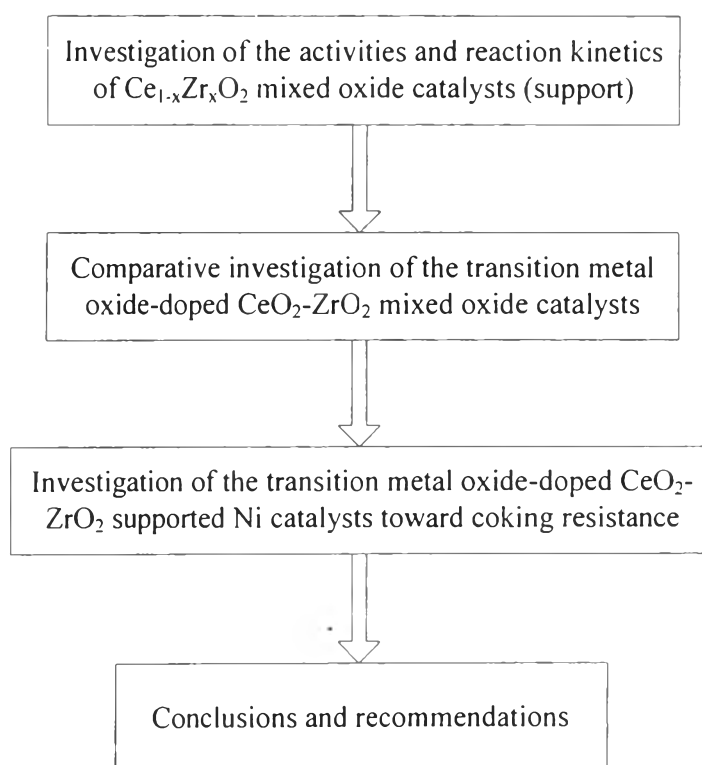
Conclusions and recommendations

Figure 1.1 Thesis overview

The general overview of tar compound, tar removal technologies and the catalysts used for tar elimination is provided in Chapter 2. Chapter 3 describes the various experimental techniques utilized for the catalyst preparation, catalyst characterizations, and reaction studies. Details of the catalytic activity test system are also given. The investigation of the naphthalene total oxidation activity over $Ce_{1-x}Zr_xO_2$ mixed oxide catalysts is described in Chapter 4. In this chapter, the

kinetic analysis over the most active catalyst and reaction kinetic expressions are also purposed. In order to better understand the role of reducibility on catalytic activity of CeO_2-ZrO_2-based mixed oxide catalysts, the information of the effect of transition metal oxide-doped CeO_2-ZrO_2 mixed oxide catalysts, $Ce_{0.75}Zr_{0.15}Me_{0.10}O_2$ (Me = Cr, Fe, Mn and V), for benzene, toluene and naphthalene total oxidation is provided in Chapter 5. Furthermore, the doping effect of the transition metal oxides (chromium, iron, manganese, and vanadium) on the steam reforming catalytic activity and carbon formation resistance, the steam reforming of toluene over nickel supported on transition metal oxide-doped CeO_2-ZrO_2 catalysts, $Ni/Ce_{0.75}Zr_{0.15}Me_{0.10}O_2$ (Me = Cr, Fe, Mn and V), is given in Chapter 6. Chapter 7 describes the effect of doping manganese on the steam reforming of naphthalene towards carbon formation resistance over nickel supported on $Ce_{0.75}Zr_{0.25-x}Mn_xO_2$ mixed oxide catalysts. Finally, in Chapter 8, the overall conclusions of this thesis are provided along with some recommendations for future research.