CHAPTER II
LITERATURE REVIEW

In this chapter, the introduction of tar and the technologies for tar elimination are provided, and the relevant works in catalytic tar removal are reviewed.

2.1 Background

2.1.1 Tar Classification

Tar is a complex mixture of condensable hydrocarbons, which includes single ring to multiple ring aromatic compounds along with other oxygen containing hydrocarbons and complex polycyclic aromatic hydrocarbons. Different approaches of tar classification are reported in the literature. Milne and coworkers (Milne *et al.*, 1998) classified tar in four different groups depending on the reaction regimes as shown in Figure 2.1. These four groups are: primary products which are characterized by cellulose-derived, hemicellulose-derived and lignin-derived products; secondary products which are characterised by phenolics and olefins; alkyl tertiary products which are mainly methyl derivatives of aromatic compounds; condensed tertiary products which are polycyclic aromatic hydrocarbons (PAHs) without substituent groups. Corella and coworkers (Corella *et al.*, 2000) grouped all the tar species in six groups, namely benzene, 1-ring compound, naphthalene, 2-ring compounds, 3- & 4-ring compounds and phenolic compounds. In another approach tar is considered as all organic contaminants with a molecular weight larger than benzene which are classified into five classes as shown in Table 2.1. This classification is mainly based on solubility and condensability of different tar compounds, rather than reactivity of the compounds.

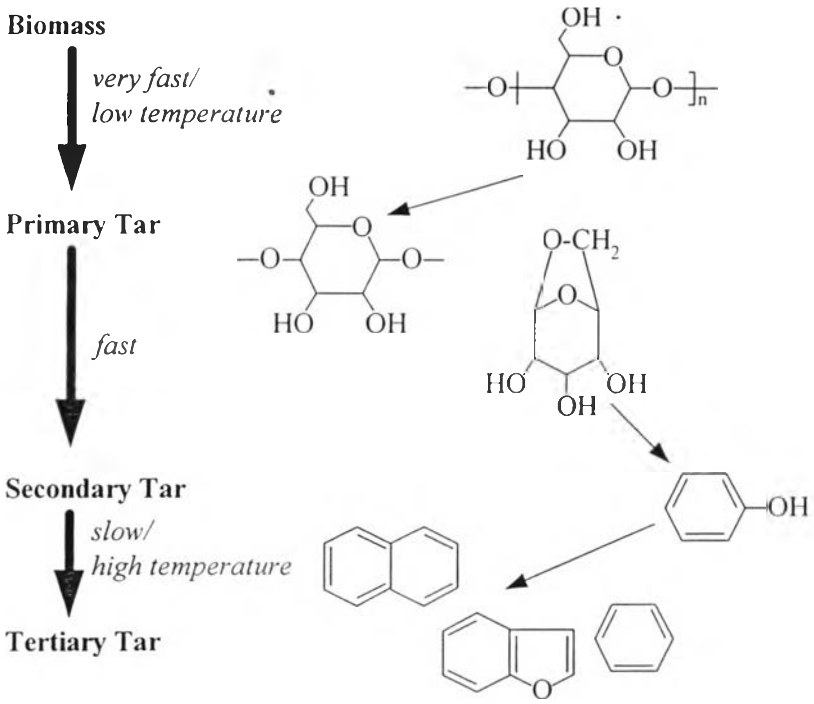

Figure 2.1 Tar classes (Milne *et al.*, 1998).

Table 2.1 List of tar compounds that are considered for different tar classes (Devi *et al.*, 2005)

Tar class	Class name	Property	Representative compounds
1	GC-undetectable	Very heavy tar, cannot be detected by GC	None
2	Heterocyclic	Tar containing hetero atoms; highly water soluble compounds	Pyridine, phenol, cresols, quinoline, isoquinoline, dibenzophenol
3	Light aromatics	Usually light hydrocarbons with single ring; do not pose a problem regarding condensability and solubility	Toluene, ethylbenzene, xylenes, styrene
4	Light polyaromatics	Two and three ring compounds; condense at low temperature even at very low concentration	Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene
5	Heavy polyaromatics	Larger than three rings; these components condense at high temperatures, at low concentrations	Fluoranthene, pyrene, chrysene, perylene, coronene

2.1.2 Tar Removal Techniques

Tar can create problems in integrated biomass gasification systems for a number of reasons. It can condense in exit pipes and on particulate filters leading to blockages and clogged filters. It also has various impacts on other downstream application processes associated with formation of tar aerosols and polymerization to form complex structures leading to problems in the subsequent process equipment. Moreover, it is dangerous since it is a carcinogenic and/or mutagenic substance (Abu El-Rub *et al.*, 2004). Typically, the amount of tar which produces from updraft, fluidized bed and downdraft gasifier are about 100, 10 and 1 g/m^3 respectively. But for the downstream application, the allowable tar levels are about 50, 5 and 1 mg/m^3 for gas engines, gas turbines and fuel cells, respectively (Iverson *et al.*, 2004). Table 2.2 shows a typical composition of biomass tar. However, this composition depends on the type of fuel and the gasification process.

Table 2.2 Typical composition of biomass tar (Coll *et al.*, 2004)

Composition	wt%
Toluene	24
Other 1-ring aromatic hydrocarbons	22
Naphthalene	15
Other 2-ring aromatic hydrocarbons	13
3-ring aromatic hydrocarbons	6
4-ring aromatic hydrocarbons	1
Phenolic compounds	7
Heterocyclic compounds	10
Others	2

In general, tar can be removed by physical, noncatalytic (i.e., thermal cracking), and catalytic tar elimination processes. If the end use of the gas requires cooling to near ambient temperature it is possible to use a number of physical removal methods, including wet scrubbing and filtration, to remove tar. Wet scrubbing is an effective gas conditioning process that condenses the tar out of the product gas. This technology is available and can be optimized for tar removal. However, a disadvantage of wet scrubbing for product gas conditioning is the formation and accumulation of wastewater. This technique does not eliminate tar but merely transfers the problem from the gas phase to the condensed phase. Also, when tar is removed from the product gas stream, its fuel value is lost and the overall efficiency of the integrated gasification process is reduced.

If the end use requires that the product gas remains at high temperatures, at or below the gasifier exit temperature, then some methods of hot gas conditioning will be needed for tar elimination. Hot gas conditioning eliminates tar by converting it into desired product gas components thus retaining its chemical energy in the product gas and avoiding treatment of an additional waste stream. Thermal cracking is a hot gas conditioning option but it requires higher temperature than a typical gasifier exit temperature (> 1,100 °C) to achieve high conversion efficiencies. Thermal destruction of tar may also produce 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 while maintaining the product gas purity.

Catalytic tar conversion is technically and economically interesting approach for gas cleaning. Such an approach is intuitively interesting because it has the potential to increase conversion efficiencies while simultaneously eliminating the need for the collection and disposal of tar. The research on catalytic tar conversion involves two methods as shown in Figures 2.2 and 2.3 (Devi *et al.*, 2003). One approach involves incorporating or mixing a catalyst with feed biomass to achieve so-called catalytic gasification. This method is one of the primary methods used for tar reduction, where the tar is being removed in the gasifier itself. In the secondary approach, the gasifier producer gas is treated at downstream of the gasifier in a secondary reactor. This method is one of the secondary methods used for tar reduction, where the tar is being removed outside the gasifier.

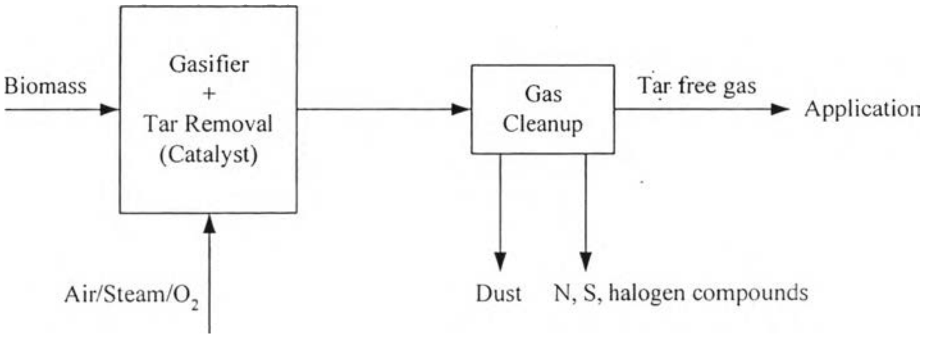

Figure 2.2 Tar reduction concept by primary methods.

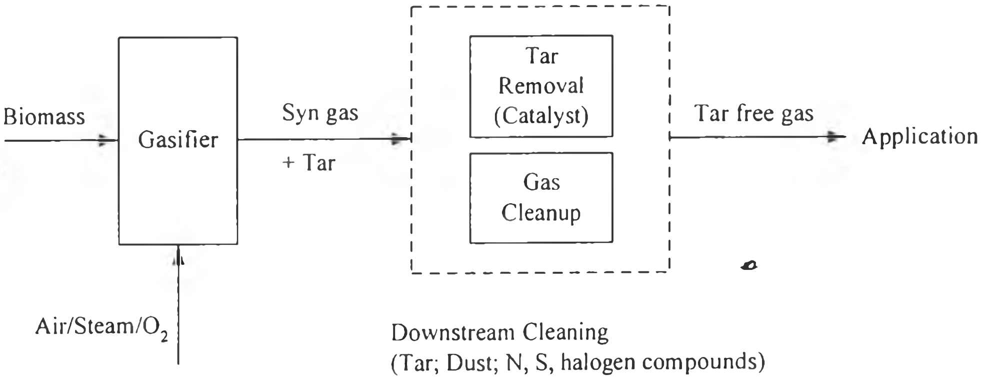

Figure 2.3 Tar reduction concept by secondary methods.

2.2 Literature Survey

2.2.1 Catalysis for biomass gasification

Catalysts for use in biomass conversion may be divided into two distinct groups which depend on the position of the catalytic reactor relative to that of the gasifier in the gasification process. The first group of catalysts (primary catalysts) is added directly to the biomass prior to gasification. These catalysts primarily have the propose of reducing the tar content and have little effect on the conversion of methane and C_{2-3} hydrocarbons in the product gas. The second group of catalysts is placed in a secondary reactor downstream from the gasifier. Independent of the type of gasifier, they can be operated under different conditions from those of the gasification unit.

Typically, three groups of catalyst materials have been applied in biomass gasification systems: alkali metals, nonmetallic oxides or calcined rocks, and transition metals catalysts (Sutton *et al.*, 2001; Devi *et al.*, 2003; Abu El-Rub, 2004).

2.2.1.1 Alkali Metal-based Catalysts

Alkali metals are any of the monovalent metals lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr), belonging to group 1A of the periodic table. Alkali metals are thought to enhance the biomass gasification reaction and therefore are considered primary catalysts and not tar reforming catalysts. These catalysts are often added directly to the biomass by dry mixing or wet impregnation. Lee and coworkers (Lee *et al.*, 2000) reported that the addition of Na_2CO_3 enhances the catalytic gasification of rice straw over nickel catalyst and significantly increases the formation of gas, which is depended on the nature of the alkali metal carbonate used and has the order $Na \geq K > Cs > Li$. The same authors also found that the catalytic activity of single salts in steam gasification depends on the gasification temperature, with the following order of activity: $K_2CO_3 > Ni(NO_3)_2 > K_2SO_4 > Ba(NO_3)_2 > FeSO_4$ (Lee, 1995). Douglas *et al.* (Douglas *et al.*, 1986) used 8 wt.% potassium carbonate as bed additive impregnated on wood for steam gasification. They observed a reduction of phenolic tar compounds by a factor of 5 and PAH by a factor of about 10. Gebhard *et al.* (Gebhard *et al.*, 1994) investigated a catalyst specifically for tar destruction, which is referred to as DN-34. They reported that the catalyst exhibit steam reforming activity for aromatic and polynuclear aromatic hydrocarbons, however, less effective for benzene and toluene destruction.

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. It also gives an increase in the ash content remaining after char gasification, and the disposal of this is predicted to become a problem for the technology over the coming years. This result make alkali metals unattractive gasification catalysts for commercial use (Antal *et al.*, 1995; Raveendran *et al.*, 1995; Richards *et al.*, 1991).

2.2.1.2 Nonmetallic Oxides or Calcined Rocks

These catalysts contain alkaline earth metal oxides (CaO and/or MgO). Alkaline earth metals include any of the divalent electropositive metals beryllium, magnesium, calcium, strontium, barium, and radium, belonging to group 2A of the periodic table. Calcined rocks include calcites, magnesites, and calcined dolomite. Among of these catalysts, calcined dolomite is considered the most popular cheap catalyst for tar elimination which provides relatively high tar conversion (up to 95%). The order of activity was calcined dolomite > calcite > magnesite (Delgado *et al.*, 1996). Calcined dolomite may be used as a primary catalyst, more commonly, in a downstream reactor, in which case it is often referred to as a guard bed. Karlsson *et al.* (Karlsson *et al.*, 1994) reported the successful demonstration of biomass IGCC process with involved dolomite as a bed material. The tar content observed was about 1-2 g m_0^{-3} of light tars (excluding benzene) and 100-300 mg m_0^{-3} of heavy tars. Corella and coworkers (Corella *et al.*, 1988) reported that the use of calcined dolomite inside the gasifier could decrease the tar amount from 6.5 (without dolomite) to 1.3 wt.%.

Although dolomite has been proven to be a very effective bed additive in terms of tar reduction, it has some critical limitations. The factors that cause catalytic deactivation of the calcined dolomite is related to coke formation. Coke is produced by the catalytic reactions involving tar side reactions that occur on the catalyst surface and causes deactivation of the calcined dolomite by covering their active sites and blocking their pores (Delgado *et al.*, 1996). In addition, dolomite is softer 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 fines.

2.2.1.3 Transition Metal-based Catalysts

Transition metals (group VIII) are considered as good catalysts for tar elimination and gas upgrading in biomass gasification. These catalysts accelerate steam and dry reforming of methane and hydrocarbons and water-gas shift reactions. Typical support materials of steam reforming catalysts are α-alumina, magnesia, magnesium aluminum spinel and zirconia calcined at > 1,000 °C (Rostrup-Nielsen, 1983). Using these catalysts greater than 740 °C, there is generally an increase in the hydrogen and carbon monoxide content of the exiting gas, with elimination or reduction of the hydrocarbon and methane content (Caballero *et al.*, 1997; Rostrup-Nielsen *et al.*, 1993). Among of transition metals, 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). Olivares *et al.* (Olivares *et al.*, 1997) reported that commercial nickel-based catalysts are 8-10 times more active than calcined dolomites under the same operating conditions. However, the major problem with Ni-based catalysts is fast deactivation due to carbon deposition on the catalyst (Srinakruang *et al.*, 2005; Wang *et al.*, 1996; Rostrup-Nielsen, 1983).

Table 2.3 shows the summary of the catalysts advantages and disadvantages for tar elimination and a brief overview of all the catalyst investigations using model biomass tar compounds reported in the literature are also listed in Table 2.4.

Table 2.3 Summary of catalysts advantages and disadvantages (Abu El-Rub *et al.*, 2004)

Catalyst	Advantages	Disadvantage
Calcined rocks	inexpensive and abundant attain high tar conversion ~95% conversion with dolomite often used as guard beds for expensive catalysts most popular for tar elimination	fragile materials and quickly eroded from fluidized beds
Olivine	inexpensive, high attrition resistance	lower catalytic activity than dolomite
Clay minerals	inexpensive and abundant fewer disposal problems	lower catalytic activity than dolomite most natural clays do not support the high temperature (800-850 °C) needed for tar elimination (lose pore structure)
Iron ores	inexpensive abundant	rapidly deactivated in the absence of hydrogen lower catalytic activity than dolomite
Char	inexpensive, natural production inside the gasifier high tar conversion, comparable to dolomite	consumption because of gasification reactions
FCC	relatively inexpensive but not cheaper than the above more known about it from experience with FCC units	rapid deactivation by coke lower catalytic activity than dolomite

Table 2.3 Summary of catalysts advantages and disadvantages (Continued)

Catalyst	Advantages	Disadvantage
Alkali-metal-based	natural production in the gasifier reduce ash-handing problems	particle agglomeration at high temperatures lower catalytic activity than dolomite
Activated alumina	high tar conversion comparable to that of dolomite	rapid deactivation by coke
Transition-metal-based	able to attain complete tar elimination at ~900 °C increase the yield of CO_2 and H_2 Ni-based catalysts are 8-10 times more active than dolomite	rapid deactivation because of sulfur and high tar content in the feed relatively expensive

Table 2.4 Overview of literature on decomposition of model biomass tar

Model tar	Catalyst	Operation Conditions	Tar concentration	Reference
Naphthalene	Dolomite	T=800-900°C	7.5-8 g	Aldén *et al.*, 1994
n-Heptane	Limestone, Dolomite,	T=750-900°C	2.4-7 kPa	Taralas, 1996
	$NiMo/\gamma\ Al_2O_3$	P=1 atm		
Naphthalene	None	T=700-1400°C	0.25-1 vol%	Jess, 1996b
Toluene		P=1.6 atm	0.6 vol%	
Benzene			0.3-1.2 vol%	
Naphthalene	Ni-MgO	T=450-950°C	0.2-0.8 vol%	Jess, 1996a
Benzene		P=1.6 atm	0.2-0.23 vol%	
Benzene	Dolomite	T=500-900°C	50-500 ppmv	Simell *et al.*, 1997a
Toluene	Al_2O_3, Dolomite,	T=900°C	720 ppmv	Simell *et al.*, 1997b
	$Ni\text{-}Al_2O_3$, SiC	P=20-50 atm		
Benzene	Dolomite	T=750-900°C	40-3400 ppmv	Simell *et al.*, 1999
		P=1 atm		

Table 2.4 Overview of literature on decomposition of model biomass tar (Continued)

Model tar	Catalyst	Operation Conditions	Tar concentration	Reference
Benzene	Ni-MgO	T=450-1150°C	0.05-1 vol%	Depner and Jess, 1999
		P=15 atm	0.1-1.4 vol%	
Naphthalene	Ni-activated candle filter	T=750-900°C	5 g m^{-3}	Zhao *et al.*, 2000
Antracene	UCI G90-C,	T=700-850°C	0.075 g min^{-1}	Coll *et al.*, 2001
Benzene	ICI 46-1		0.67 g min^{-1}	
Naphthalene	(Ni-based)		0.076-0.123 g min^{-1}	
Pyrene			0.033 g min^{-1}	
Toluene			0.68 g min^{-1}	
Naphthalene	Co/MgO	T=900°C	1.0 g h^{-1}	Furusawa *et al.*, 2005
	Ni/MgO			
Naphthalene	Ni-dolomite	T=700°C	-	Wang *et al.*, 2005
Toluene	Ni/Mayenite	T=500-800°C	2000 ppm	Li *et al.*, 2009
	$Ni/CaO_x/MgO_{1-x}$			

Based on the reported literature. Ni-based steam reforming catalysts have proven to be useful in biomass gasification for gas cleaning and upgrading. The main advantages of Ni-based catalysts are their ability to attain complete tar elimination at temperature around 700-900 °C and increase the yields of CO and H_2. A limitation of nickel catalyst use for hot gas conditioning of biomass gasification is rapid deactivation due to carbon formation, which leads to loss of tar catalyst activity. As a result. there is considerable interest in minimizing coke formation: how this may be done is the subject of the text below.

2.2.2 Strategies for Coke Minimisation

Carbon formation promoted by a catalyst is more complex and is harder to minimise. It occurs on the catalyst surface, and the process is fairly well understood. It is believed that hydrocarbons dissociate on the nickel surface to produce highly reactive carbon species (C_α) which are probably atomic carbon (McCarty *et al.*,, 1979; Bartholomew, 1982). C_α is easily gasified, however, if there is excess of C_α formed or gasification is slow, then polymerisation to C_β is favoured. The carbon may be gasified, may dissolve in the nickel crystallite, or may encapsulate the surface. The dissolved carbon diffuses through the nickel to nucleate and precipitate at the rear of the crystalline. This continuting process leads to the formation of carbon whisker, which lifts the nickel crystallite from the catalyst surface, and eventually results in fragmentation of the catalyst (Trimm, 1977; Rostrup-Nielsen, 1977). Not all of the coke formed on the surface dissolves in nickel. At least some carbon remains on the surface and encapsulates nickel (Trimm, 1977; Rostrup-Nielsen. 1977).

2.2.2.1 Ensemble Size Control

The first approach rests on the concept of ensemble size control (limiting the number of near-neighbour active sites) (Rostrup-Niesen, 1991). Rostrup-Niesen argued that coke formation would require an ensemble of surface sites that would be larger than that required for reforming. The formation of carbon – either dissolved in or deposited on the nickel–must require the polymerisation of monoatomic carbon species (C_α), while gasification involves only one such species. As a result, it was reasoned that, by controlling the number of sites in an ensemble, it may be possible to minimise coking whilst maintaining reforming activity. The basis of the ensemble size control, for example, adsorption of small amounts of sulphur on nickel. Under these conditions, the rate of steam reforming was reduced but coke formation was essentially eliminated.

2.2.2.2 Preventing Carbide Formation

Carbide was suggested to be the essential intermediate en route to coke. It was reasoned that prevention of carbide formation on the surface could slow down the whole process of coke formation, since dissolution and precipitation could probably only occur via carbide formation. Trimm (Trimm, 1991) suggested that the electronic structure of carbon is very similar to the electronic structure of the tetra- and penta-valent p metals (such as Ge, Sn and Pb or As, Sb or Bi) and of sulphur. With carbon, nickel carbide is formed from the interaction of 2p electrons from the carbon with the 3d electrons of the nickel. Thus it would seem possible that tetra- or penta-valent p metals could also interact with Ni 3d electrons, thereby reducing the chance of nickel carbon formation.

2.2.2.3 The Use of Alternative Supports

Minimisation of coking is also a function of support, and here attention has been focused recently on the role of metal oxides (Bona *et al.*, 2007; Wang *et al.*, 2006; Zhang *et al.*, 2006; Miyazawa *et al.*, 2006; Furusawa and Tsutsumi, 2005).

Miyazawa (Miyazawa *et al.*, 2006) studied the activity of Ni/Al_2O_3, Ni/ZrO_2, Ni/TiO_2, Ni/CeO_2 and Ni/MgO catalysts (12 wt.% of nickel) in the partial oxidation (POT) and steam reforming of tar (SRT) derived from the pyrolysis of cedar wood. They reported that the order of the performance in both reactions is similar (Ni/Al_2O_3 > Ni/ZrO_2 > Ni/TiO_2 > Ni/CeO_2 > Ni/MgO > no catalyst). They also suggested that the conversion of tar in POT and SRT is mainly controlled by the number of surface Ni metal, and the role of the support materials is for the dispersion of Ni metal. Regarding coke amount, Ni/CeO_2 showed smaller amount of coke than other catalysts in the POT and SRT, it is suggested that, Ni/CeO_2 promoted the reaction of active carbon with O_2 and steam.

Sánchez-Sánchez (Sánchez-Sánchez *et al.*, 2007) investigated the influence of the support on ethanol steam reforming over Ni/M_xO_y-Al_2O_3 (M = Ce, La, Zr and Mg). They reported that the higher reforming activity for Mg-modified catalyst respect to bare Al_2O_3 was explained in terms of the lower acidity and better dispersion achieved in the former, while for Ce- and Zr-promoted catalysts the improvement in intrinsic activity was ascribed to the enhancement of water adsorption/dissociation on the Ni-Ce and Ni-Zr interfaces developed on these catalysts. La and Ce additives were found to prevent the formation of carbon filaments on nickel surfaces.

As the literature data, the redox property and the mobility of the surface oxygen and/or OH groups of support seems important factors for enhance of tar catalyst activity and minimise the carbon deposition. In addition, thermal stability of the catalysts is also important, particularly since the Tammann temperature, above which nickel sintering can be expected (590 °C), is less than the normal operating temperatures (ca. 700-900 °C) for reforming reaction (Trimm, 1991). The use of support not only offers an opportunity for assistance with carbon deposition control but also induces thermal stability.

2.2.3 Ceria- Zirconia Mixed Oxides

Cerium oxide (CeO_2) is an important material for many applications in catalysis. This is mainly because the ceria lattice can contain a high concentration of highly mobile oxygen vacancies. These act as local sources or sinks for oxygen involved in reactions taking place on the ceria surface or on other catalytic materials supported on ceria. As a consequence, cerium oxide is a key constituent of catalysts for variety of reactions involving the oxidation of hydrocarbons. It is also noted for its ability the resist carbon deposition and to catalyse the combustion of carbon (Laosiripojana *et al.*, 2006). In addition, cerium oxide (CeO_2) has been used as a promoter in Ni-based catalysts to enhance the resistance to coke formation since the Ni-CeO_2 system has strong metal support interaction (Wu *et al.*, 1987). The role of CeO_x (x = 2 or 1.5) is to accelerate the reaction of steam with absorbed gaseous species on the nickel surface near the boundary area, so that carbon appearing on the surface can be quickly converted to gaseous products, preventing its accumulation.

Zhang (Zhang *et al.*, 2006) investigated the steam reforming of tar compounds (benzene and toluene) by using the NiO/olivine and NiO/olivine doped with CeO_2. They reported that the promotion effect of cerium oxide on the nickel catalyst is probably through a redox mechanism. The lower valence state cerium might adsorb water and dissociate it, the resulting species –O or –OH transferring to the nickel and reacting with surface carbon species to form carbon monoxide, carbon dioxide and hydrogen. Therefore, cerium oxide is a good candidate support for the eliminating of tar due to high resistance towards carbon formation.

The use of CeO_2-based catalysts has shown a rapid increase in the past decade. However, ceria still has some disadvantages. Ceria, by its self, has a poor thermal resistance and stability at high temperatures. CeO_2 has the cubic fluorite structure and foreign cations, such as Si^{4+}, Th^{4+}, Zr^{4+}, Y^{3+}, La^{3+}, Sc^{3+}, Mg^{2+}, Ca^{2+} and Cu^{2+} can be introduced into the CeO_2 lattice and can improve the physical properties of the CeO_2. Particularly, partial substitution of Ce^{4+} with Zr^{4+} in the lattice of CeO_2, which results in a solid solution formation, leads to improvements in its oxygen storage capacity, redox properties and thermal resistance as well (Hori *et al.*, 1998; Fornasiero *et al.*, 1995). Nevertheless, it was also reported that CeO_2-ZrO_2 solid solutions showed a high catalytic activity, particularly for oxidation of CO, CH_4 and for partial oxidation of *iso*-octane (Thammachart *et al.*, 2001; Pengpanich *et al.*, 2002; Pengpanich *et al.*, 2006). A high oxygen mobility, thermal resistance and strong interaction with the supported metal (SMSI) render the CeO_2-based materials very interesting for catalysis and as a support (Fornasiero *et al.*, 1996; Fan *et al.*, 1997).