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DEVELOPMENT AND EVALUATION OF HETEROGENEOUS CATALYSTS TO CONVERT BIOMASS TO USEFUL CHEMICALS

By

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A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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ABSTRACT

Hydrogen is the environmentally friendly fuel and production of hydrogen from biomass, a renewable resources, is an alternative to conventional hydrogen production from petroleum and natural gas. Gasification of biomass represents an efficient way to generate energy with high efficiency and low environmental impacts. In the pyrolysis of biomass, 50-70 wt% of product fraction is the organic fraction/tars that may cause problems in downstream equipment. Catalytic steam reforming process appears promising, because it can convert tar into synthesis gas at the same or even lower temperature than the gasification, which will improves the carbon efficiency and entire process efficiency. Ni-based catalyst received the most attention for industrial applicable steam reforming catalyst. However, easily catalyst deactivation through metal sintering and coke deposition is considered the major challenge to be addressed. Although many efforts have been conducting by modifying the chemical composition of catalyst support or/and by promoting the catalyst with additives, the development in more stable Ni-based catalysts with high resistance to coke deposition and sintering are still required.

In this study, catalytic steam reforming of biomass derived-tar (CSRT-biomass) was firstly investigated with the supported transition metal catalysts (Ni/SiO$_2$, Co/SiO$_2$, Fe/SiO$_2$, and Ni/SBA-15). Commercial fume silica was used as SiO$_2$ support, and regular pore size SBA-15 support (avg. pore size: 4.8 nm) was synthesized by a soft template procedure using surfactant (triblock copolymer Pluronic P123; PEO20PPO70PEO20). The supported catalysts were synthesized by a precipitation procedures, and characterized by N$_2$ adsorption-desorption and X-ray diffraction (XRD). The catalytic activity experiment was evaluated in a single-stage fixed-bed reactor (ID = 8 mm × L = 500 mm) under the 50 mL/min of N$_2$ carrier gas flow. In the study of activity of the 10Ni/SiO$_2$, 10Co/SiO$_2$, 10Fe/SiO$_2$ catalysts, 10Ni/SiO$_2$ catalyst showed higher performance than 10Co/SiO$_2$ and 10Fe/SiO$_2$ catalysts. The effect of the metal loading (10 wt%, 20 wt% and 30 wt%) and support (SiO$_2$ and SBA-15) were also examined on Ni/SiO$_2$ and Ni/SBA-15 catalysts. As the results, 20 wt% metal loaded catalysts exhibited higher performance than 10 and 30 wt% loaded catalysts. SBA-15 supported catalysts showed higher activity than SiO$_2$ supported catalysts.

For the development of a more stable Ni-based catalyst with high resistance in carbon deposition and sintering, modification of the Ni/SBA-15 catalyst was attempted by adding MnO$_x$ to Ni metal. Additionally, modification on SBA-15 support and catalyst preparation technique were also attempted. Large pore size SBA-15 (avg. pore size: 7.66 nm) was synthesized and used as a catalyst support in order to reduce mass transfer resistance. Catalyst were synthesized via ethylene glycol (EG) assisted impregnation technique. The catalytic activities of the Ni-MnO$_x$/SBA-15 catalysts were evaluated by a two-stage fixed-bed reactor system in order to separately control the pyrolysis bed and the catalyst bed.

Large pore SBA-15 (avg. pore size: 7.66 nm) supported Ni, MnO$_x$, and Ni-MnO$_x$ catalysts were prepared via ethylene glycol (EG) assisted impregnation technique. The catalysts were characterized by N$_2$ adsorption-desorption, XRD, transmission electron
microscope (TEM) and temperature program reduction (TPR), and the amount of carbon deposition on the used catalysts were determined by temperature program oxidation (TPO). All of the catalysts showed small metal particle size (< 5nm) and high dispersion into the porous channel of the SBA-15 framework, according to analysis results (TEM and TPR). In the catalytic steam reforming experiments, the activities of the Ni-MnOx/SBA-15 catalysts showed as high as that of the Ni/SBA-15 catalyst while MnOx/SBA-15 catalyst exhibited low activity. Addition of small amount (1 wt%) of Mn to Ni (9Ni-1Mn/SBA-15) catalyst exhibited higher performance in term of product gas formation and H2 yield than the corresponding monometallic 10Ni/SBA-15 catalysts. It was due to increased dispersion of Ni species by Mn addition, and the synergy effect between Ni metal and MnOx in which MnOx supply of O2 to active Ni species, which promoted the reaction between carbonaceous species and oxygen species on the Ni surface. H2 formation rates of the catalysts in these experiments were significantly higher than the other recently reported catalytic steam reforming works. Furthermore, very low carbon deposition amounts (< 1 wt%) and complete tar conversions were observed in 10Ni/SBA-15 and 9/7/5Ni-1/3/5Mn/SBA-15 catalysts.

It has been known that metal-support interaction (MSI) is one of the important factors on catalytic activity and stability. Calcination temperature in synthesize of catalyst is one parameter to enhance MSI. In this study, Ni-MnOx/SBA-15 catalysts were calcined at two different temperature (723 K and 973), and relation between MSI and catalytic activity of Ni-MnOx/SBA-15 was investigated. The calcined catalysts were characterized by N2 adsorption-desorption, XRD, TEM and TPR, and used catalysts were analyzed by TPO and XRD. Catalytic steam reforming experiments were performed in a two-stage fixed-bed reactor. As the results of activity tests, higher temperature calcined catalysts (10Ni/SBA-15-C973 and 9Ni-1Mn/SBA-15-C973) showed higher performance than low temperature calcined catalysts (10Ni/SBA-15-C973 and 9Ni-1Mn/SBA-15-C973). This indicates the presence of Ni2SiO4 and NiMn2O4 phases in the Ni-MnOx/SBA-15-C973 catalysts play important role in the activity and H2 formation in CSRT-biomass reaction, expecting that spillover effect was occurred in these phases. Moreover, carbon deposition amounts on used catalysts were very low and crystallite sizes of the used catalysts were not become larger after the activity tests, indicates as stable catalysts. The 9Ni-1Mn/SBA-15-C973 catalyst showed the highest activity in term of product gas formation and 10Ni/SBA-15-C973 catalyst resulted in highest H2 formation amount.

The Ni-MnOx/SBA-15 catalysts can be expected as highly stable catalysts, considering from carbon deposition amounts and XRD results of the used catalysts. Finally, the prepared catalysts can be the potentially applicable as the tar steam reforming catalysts.
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CHAPTER 1

INTRODUCTION

1.1 Background

Hydrogen’s share in the energy market is increasing with the implementation of fuel cell systems and the growing demand for zero-emission fuels. Approximately 95% of hydrogen produced today is from fossil fuel sources. Renewable-based processes like solar or wind-driven electrolysis and photo-biological water splitting hold great promise for clean hydrogen production; however, advantages must still be made before these technologies can be economically competitive. Hydrogen from biomass may be the more practical and viable, renewable and potentially carbon-neutral option.

Biomass has the potential to accelerate the realization of hydrogen as a major fuel of the future. Since biomass is a renewable and consumes atmospheric CO\textsubscript{2} during growth, it can have a small net CO\textsubscript{2} impact compared to fossil fuels. Conversion of biomass to hydrogen can be processed by thermochemical and biological routes as shown in Figure 1.1. Generally, thermo-chemical processes have higher efficiencies than biochemical/biological processes in terms of the low reaction time required (a few seconds or minutes for thermo-chemical processes vs. several days, weeks or even longer for biochemical/biological processes).

Gasification of biomass represents an efficient way to generate energy with high efficiency and low environmental impacts. Gasification is a two-step process in which a solid fuel (biomass or coal) thermo-chemically converted to a low or medium energy content gas. In the first reaction (reaction (1)), pyrolysis, the dissociated and volatile components of the fuel are vaporized at temperature as low as 600°C. Included in the volatile vapors are hydrocarbon gases, H\textsubscript{2}, CO, CO\textsubscript{2}, tar and water vapors. In the second stage (reaction (2)-(10)), the char is gasified through the reactions with O\textsubscript{2}, steam and H\textsubscript{2}.

\begin{align*}
C_nH_mO_x &\rightarrow CO + CO + H_2O + CH_4 + H_2 + (C_2-C_5) + \text{tars} \quad (1) \\
C + O_2 &\rightarrow CO_2 \quad (2) \\
C + \frac{1}{2} O_2 &\rightarrow CO \quad (3) \\
H_2 + O_2 &\rightarrow H_2O \quad (4) \\
C + H_2O &\rightarrow CO + H_2 \quad (5) \\
C + 2H_2O &\rightarrow CO_2 + 2H_2 \quad (6) \\
C + CO_2 &\rightarrow CO \quad (7) \\
C + H_2 &\rightarrow CH_4 \quad (8) \\
CO + 3H_2 &\leftrightarrow CH_4 + H_2O \quad (9) \\
C + H_2O &\rightarrow \frac{1}{2} CH_4 + \frac{1}{2} CO_2 \quad (10)
\end{align*}

Reaction (2)-(4) are oxidation reactions that occur in the presence of oxygen. Since reaction (2) and (3) are exothermic, enough heat is generated to dry the feedstock, to break up the chemical bonds (pyrolysis of biomass), and to maintain a high temperature for the gasification reactions. Among these, reaction (2) has the greatest energy release. In contrast, the heat generation capacity of reaction (3) is only 65% of that of the reaction (2). Reactions (5) and (6) are the main gasification reactions; they are water gas reactions. Reaction (9) is the methanation, it proceeds slowly at low temperature and in the absence of any catalysts. In the pyrolysis of biomass, 50-70wt% of product fraction is the organic fraction/tars that may cause problems in downstream equipment. Removal of tar can be accomplished through several routes, including common physical separation technologies, such as filtration and aqueous or organic liquid.
scrubbing. Although these unit operations may be effective, they require significant heating and cooling steps unless the gas is decreased the overall process efficiency. In addition, liquid scrubbing produces large amounts of liquid waste/wastewater that requires downstream treatment and/or recycle. Thermal cracking can remove most of the tars present in syngas, although cracking efficiency improves with temperatures that are significantly higher (>1100°C) than typical biomass gasification temperatures, which again imposes a heat penalty.\(^5\) Compared to physical separation and thermal cracking, catalytic tar conversion appears more promising, because it can convert tar into synthesis gas at the same or even lower temperature than the gasification and without the production of wastewater, which will improves the carbon efficiency and entire process efficiency.

![Biogas Resource Pathway](image)

**Figure 1.1.** Pathway for biomass to hydrogen; storable intermediates are shown in boxes.

There are several manufactures for reforming of methane and higher hydrocarbons and a number of these catalyst suppliers are listed in Table 1.1. These catalysts are normally designed for specific application within natural gas or naphtha reforming industries. The behavior of some of these catalysts has been studied in biomass gasification but in air blown conditions and mostly within atmospheric applications. There is a lack of long term experiences from the test of these catalysts in biomass product gas environment which is characterized with high concentration of tars, moderate content of sulphurous and chlorinated compounds.\(^6\) For steam reforming, Ni or noble metals Ru, Rh, Pd, Ir, Pt are used as active metal in catalysts. Because of its low cost, Ni is the most widely used metal from this set.\(^7\)

The most commonly used support for commercial Ni steam reforming catalysts has been alumina (Al\(_2\)O\(_3\)). Alumina has worked well for natural gas (methane) steam reforming (SMR) catalysts, but biomass-derived syngas contains a wide range of impurities that negatively influence the activity of conventional SMR catalysts. The other commonly used supports in this kind of catalysts are MgO, SiO\(_2\), ZrO\(_2\), ZnO, TiO\(_2\) and CeO\(_2\). These supports have good porosity, which results in a long-contact time between reactant and catalysts. Maintaining a high surface area is important: the support
can affect the migration and coalescence of metal particles (ie., sintering) in various ways. Pore structure, morphology and phase transitions of the support determine the final particle size of the metal. But there is more. Obviously, due to the nature of chemical bonding between the support and the metal atoms, the electronic properties—and hence the reactivity of the metal—is affected. For instance, acidity in the support is known to facilitate the decomposition of methane, but it will also enhance cracking and polymerization, producing carbon.

<table>
<thead>
<tr>
<th>Company</th>
<th>Application</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASF</td>
<td>Tar/ammonia reduction, steam reforming, shift</td>
<td>Granulate, monolith</td>
</tr>
<tr>
<td>Ecocat/Kemira</td>
<td>Environmental application, trace gas reduction</td>
<td>Metallic support</td>
</tr>
<tr>
<td>Alvigo ltd</td>
<td>Reforming of naphtha and methane, ammonia synthesis, H₂S removal---</td>
<td>Catalyst on Dycat support (ceramic), also on monolith</td>
</tr>
<tr>
<td>ICI (catalco)</td>
<td>Naphtha reforming</td>
<td>Ni-catalysts supported on ceramic rings</td>
</tr>
<tr>
<td>Holder Topsoe</td>
<td>Methanation, steam reforming</td>
<td>Ni- based on ceramic rings and pellets, even with high sulphur tolerance</td>
</tr>
<tr>
<td>Alvigo ee/</td>
<td></td>
<td></td>
</tr>
<tr>
<td>InnovaTec</td>
<td>Steam reforming of natural gas, diesel----</td>
<td>High sulphur tolerance, fuel cell application</td>
</tr>
<tr>
<td>Norta</td>
<td>Different applications within reforming and environmental</td>
<td>Transition metals on metallic film, plasma sprayed</td>
</tr>
<tr>
<td>NORTA, UAB Savanorių pr. 290, LT-KAUNAS</td>
<td>Naphtha reforming, steam reforming</td>
<td>Ni-catalysts on ceramic rings</td>
</tr>
<tr>
<td>United catalysts (Shed Chemic)</td>
<td>Naphtha reforming, steam reforming</td>
<td></td>
</tr>
</tbody>
</table>

However, Ni is more prone to deactivation by carbon formation or oxidation. Most research in this field is still focusing on improving performance of Ni based catalysts. More specifically, by modifying the chemical composition of the catalyst support or by promoting the catalyst with “additives”, one aims at achieving longer lifetime (ie., stability, reducing coke formation) and higher activity (e.g., at lower temperatures). The influential factors on the catalyst activity and stability are found to be the metal particle size and dispersion, strong metal-support interaction and the catalyst reducibility. Furthermore, the major challenge to be addressed for development of industrial applicable Ni-based steam reforming catalyst was deactivation of catalyst through metal sintering and coke deposition.

To overcome carbon deposition on Ni catalysts, many Ni-based bimetallic catalysts such as Ni-CeO₂, Ni-Co, Ni-Cu, Ni-Fe, and Ni-Mn have been developed. The improvement in catalytic performance of bimetallic was related to the formation of alloy particles and/or supply of oxygen from the second metal to the Ni metal. MnOₓ containing catalysts have been widely applied in many reactions, including NOₓ reduction, and steam reforming, owing to its excellent redox property. Koike et al. synthesized Ni/MnOₓ/Al₂O₃ catalysts by co-impregnation method and the performance of the catalysts were studied in the CSRT-biomass reaction.
They reported that Ni/MnOₓ/Al₂O₃ catalysts showed higher performance than Ni/CeO₂/Al₂O₃ catalysts. The supply of oxygen atoms from MnOₓ to Ni species enhanced the reaction between carbonaceous and oxygen on the Ni. Therefore, MnOₓ is a very interesting additive for the development of Ni-based steam reforming catalysts.

It has been known that strong metal-support interaction (SMSI) is one of the important factors on catalytic activity and stability. The steam reforming catalyst with SMSI such as Ni/Mg/Al, Ni-Fe/Mg/Al and Ni-Cu/Mg/Al by using hydrotalcite-like compounds, was recently developed and reported. D. Li et al. reported that formation of nanocomposite in the Ni/Mg/Al catalyst enhanced the interaction between the Ni metal particle and oxide support, suppressed the aggregation of metal particles and exhibited higher activity, resistance to coke deposition, and stability than Al₂O₃- and MgO-supported Ni catalysts. D. Li et al. reported that the formation of uniform Ni-Fe alloy and Ni-Cu alloy nanoparticles in the Ni-Fe/Mg/Al and Ni-Cu/Mg/Al catalysts exhibited very high activity for the steam reforming of biomass tar.

Apart from the metal oxide supported steam reforming catalysts, the supports with high surface area and large pore volume are increasing in attention. Among them, mesoporous SBA-15 material is interesting, and have been proved to be a good support to dispersing and controlling metal particle size. In addition, the strategy of stabilizing the metal nanoparticles by encapsulating into the porous channel of SBA-15 material have been explored. Therefore, the used of the SBA-15 supported Ni-based metal catalysts have been applied in many reactions, including ethanol steam reforming, steam reforming in cellulose decomposition, steam reforming of biomass tar model compound, although there are very few or no report on the catalytic steam reforming biomass derived tar (CSRT-biomass) using the SBA-15 supported Ni-based catalyst.

1.2 Objectives of this study
The main objective of this study is development of low temperature tar steam reforming catalyst with high H₂ yield. The objectives of this study are -

1. Supported transition metal catalysts (Ni, Co and Fe) are synthesized and their performance will be evaluated in the CSTR-biomass reaction.
2. Effect of support and metal loading of Ni catalysts will be studied.
3. Highly dispersed Ni-MnOₓ/SBA-15 catalysts will be synthesized by ethylene glycol (EG) assisted impregnation technique and promoting effect of Mn addition to Ni metal will study.
4. Effect of calcined temperature and pre-reduction temperature of Ni-MnOₓ/SBA-15 catalyst in CSTR-biomass will be examined and discussed.

1.3 Thesis structure
Chapter 1 is the introduction of this work. Chapter 2 describes the literature survey on properties and constituents of biomass, biomass gasification, tar problem in biomass gasification and tar removal methods, the process of the catalytic steam reforming of tar, and the steam reforming catalysts. Chapter 3 demonstrates the synthesis methods and procedures for SBA-15
materials, the supported catalyst synthesize method and procedures, catalyst analysis technique and equipment, catalytic activity tests, and experimental set up.

Chapter 4 reports the performance of the SiO$_2$ supported Ni, Co and Fe catalysts in CSRT-biomass. The effect of metal loading and support on Ni catalysts were also reported.

Chapter 5 presents the catalytic activity of Ni-MnO$_x$/SBA-15 catalyst in CSRT-biomass reaction. The enhancement in performance of Ni-MnO$_x$/SBA-15 catalysts was discussed based on the results of activity experiments and characteristics of catalysts.

Chapter 6 reports the role of metal-support interaction and catalytic activity of Ni-MnO$_x$/SBA-15 catalysts in CSRT-biomass. The effect of calcination temperature and reduction temperature of catalysts in CSRT-biomass were studied and discussed.

Chapter 7 represents conclusion and recommendations for future work.

References

3. E. David, Chemical Engineering Transactions, 2015, 43, 403-408.
CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

Biomass is an important feedstock in C1 chemistry for the production of hydrogen, liquid hydrocarbon fuels, and methanol. The main routes of producing fuels from biomass include (1) gasification to produce syngas, (2) liquefaction and pyrolysis to produce bio-oils, (3) hydrolysis to form aqueous phase sugars or lignin, which can further processed via-fermentation or reforming, and (4) transesterification of triglycerides to produce biodiesel. Among these processes, biomass gasification was attractive due to its high conversion efficiency of energy and fuel. However, tar formation during gasification was one of the primary obstacles preventing commercialization of this technology. Tars can cause several operational problems, thus blocking, fouling, corrosion, erosion and abrasion of process equipment such as engine and turbines. In addition, large amount of wastewater produces from scrubbing process that requires downstream treatment and/or recycle. Moreover, these tars are dangerous because of their carcinogenic character.

In general, tars can be removed by 1) physical process, 2) thermal, steam and partial oxidation and 3) catalytic destruction. Physical method involve filters and scrubbers, where the tar is separated in a condensed form. However, a great disadvantage of this strategy is that the crude synthesis gas needs to be cooled down before the final separation. Furthermore a huge amount of waste water is produced. In addition to that tar can be removed thermally. Thereby temperature from over 1000ºC is required to remove the undesired components completely. From the economic and technical point of view, the catalytic process therefore is a promising alternative. The great advantage of this strategy is that a high degree of purity can be achieved at low temperature and simultaneous increase of the fuel value. To meet the demands of an energy efficient process, a tar removal strategies in the temperature range from 350-700ºC is desirable. A special challenge is indeed the choice of catalyst.

Many types of catalysts have been investigated to reduce tar. Non-metallic catalysts such as dolomites, and metallic catalysts such as Ni, have been extensively study. Natural material, such as Dolomites and olivine, are inexpensive and received significantly attention for use as tar cracking catalysts. However, they showed poor activity for reforming of light hydrocarbons, such as methane, also suffer from poor attrition resistance. This attrition leads to unwanted particulates in the product stream and results in the need for frequent catalyst replacement. To improve the steam reforming activities of tar and light hydrocarbon, such as methane, researches have looked at synthetically incorporating metals, such as nickel, into natural olivine and dolomite. In the study of metal catalysts, the highest reforming activities were achieved with Ni-, Pt- and Rh-based catalysts. Although Pt and Rh have shown high reforming activity, their high cost limits their use in industrial applications. As a result of the high cost of Rh and Pt, more study have focused on Ni-based catalysts. Many studies have been published the used of Ni catalysts in the tar steam reforming reaction,
including doping with the other metals, supported on various kind of material, the catalyst synthesized by modern methods and so on. The duration of most reported catalysts have been quite short and the catalyst for long activity was still need to develop for economic and commercial application.

2.2 Biomass

Biomass is organic material that comes from plants and animals, and it is a renewable source of energy. The biomass can be collected and converted into useful bioenergy. It includes crop residues, forest and wood process residues, animal wastes including human sewage, municipal solid waste (MSW) (excluding plastics and non-organic components), food processing wastes, purpose grown energy crops and short rotation forests.

2.2.1 Constituents of biomass

Biomass includes a wide range of organic materials, which are generally composed of cellulose, hemicellulose, lignin, lipids, proteins, simple sugars and starches. Among these compounds, cellulose, hemicellulose and lignin are the three main constitutes and composition of these compound are described in Table 2.1.

<table>
<thead>
<tr>
<th>Source</th>
<th>Cellulose (%)</th>
<th>Hemicellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardwood</td>
<td>40-55</td>
<td>24-40</td>
<td>18-25</td>
</tr>
<tr>
<td>Softwood</td>
<td>45-50</td>
<td>25-35</td>
<td>25-35</td>
</tr>
<tr>
<td>Corn stover</td>
<td>38-40</td>
<td>28</td>
<td>7-12</td>
</tr>
<tr>
<td>Corn cobs</td>
<td>45</td>
<td>35</td>
<td>15</td>
</tr>
<tr>
<td>Bagasse</td>
<td>32-48</td>
<td>19-24</td>
<td>23-32</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>33-38</td>
<td>26-32</td>
<td>17-19</td>
</tr>
<tr>
<td>Rice straw</td>
<td>28-36</td>
<td>23-28</td>
<td>12-14</td>
</tr>
<tr>
<td>Sorghum stalks</td>
<td>27</td>
<td>25</td>
<td>11</td>
</tr>
<tr>
<td>Barley straw</td>
<td>31-35</td>
<td>27-38</td>
<td>14-19</td>
</tr>
<tr>
<td>Leaves</td>
<td>15-20</td>
<td>80-85</td>
<td>0</td>
</tr>
</tbody>
</table>

2.2.2 Properties of biomass

Physical properties include density, particle size and surface area and shape. Major constitute elements in biomass are carbon, oxygen and hydrogen. These element fraction can be quantified using ultimate analysis. Volatiles and fixed carbons are measured by proximate analysis. Characteristic of some basic type of biomass are showed in Table 2.2. Sawdust and wood have higher carbon content and higher heating value than the other biomass. Therefore, they are common feedstocks for biomass gasification.
Table 2.2. Chemical properties of some basic type of biomass

<table>
<thead>
<tr>
<th></th>
<th>Ultimate analysis (wt% dry basis)</th>
<th>Proximate analysis (wt% dry basis)</th>
<th>Heating values HHV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>Agricultural residues</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sawdust</td>
<td>50</td>
<td>6.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Bagasse</td>
<td>48</td>
<td>6.0</td>
<td>-</td>
</tr>
<tr>
<td>Corn cob</td>
<td>49</td>
<td>5.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Short rotating woody crops</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beech wood</td>
<td>50.4</td>
<td>7.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Herbaceous energy crops</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Switch grass</td>
<td>43.0</td>
<td>5.6</td>
<td>0.5</td>
</tr>
<tr>
<td>Straw</td>
<td>43.5</td>
<td>4.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>49</td>
<td>4.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Municipal solid waste</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry sewage</td>
<td>20.5</td>
<td>3.2</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Composition are proximate and may not sum exactly to 100%.
Biomass moisture contents reported are for dry feedstocks.
2.3 Biomass gasification

Biomass gasification is thermo-chemical process that converts carbon containing fuels, such as coal and biomass, into combustible gaseous products carbon monoxide (CO), hydrogen (H₂) and methane (CH₄); however, undesirable products like tar and char are also produced under high temperature and limited oxygen supply environment. Biomass gasification is generally acceptable to say that the major reaction include pyrolysis, oxidation, partial oxidation, reduction, steam reforming and water-gas shift reactions^1–3^ Pyrolysis is an endothermic decomposition process which takes place at high temperature in the absence of air or steam. Biomass composition mainly comprises lignin, cellulose and hemicellulose. During biomass pyrolysis, it has been identified that biomass decomposes according to the following four stages: at temperature < 493 K, moisture was evaporated; at 492-588 K, predominantly hemicellulose decomposition occurred; at 588-673 K, cellulose decomposition was observed; and at > 673 K, mainly lignin decomposed.

In oxidation or partial oxidation reactions, carbonaceous products from pyrolysis reaction may react further with oxygen to generate more gas and release heat. In the final step of gasification, product gas are upgraded through steam reforming, which converts low molecular weight hydrocarbons such as methane into H₂ and CO. Water-gas shift reaction further converts CO and steam gasification but to a lesser extent.⁵,⁶ These reaction have been summarized in Table 2.3.

Table 2.3. Gasification equations and their enthalpy for C6 compounds⁸

<table>
<thead>
<tr>
<th>Reaction name</th>
<th>Stoichiometric equation</th>
<th>ΔH° at T = 27º C and x = 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis</td>
<td>CₓHᵧOᵦ → (1-x)CO + ½H₂ + C</td>
<td>(1) 180</td>
</tr>
<tr>
<td></td>
<td>CₓHᵧOᵦ → (1-x)CO + ½H₂ + CH₄</td>
<td>(2) 71</td>
</tr>
<tr>
<td></td>
<td>CₓHᵧOᵦ + ½O₂ → xCO + ½H₂</td>
<td>(3)</td>
</tr>
<tr>
<td>Partial oxidation</td>
<td>CₓHᵧOᵦ + O₂ → (1-x)CO + CO₂ + ½H₂</td>
<td>(4) -213</td>
</tr>
<tr>
<td></td>
<td>CₓHᵧOᵦ + ½O₂ → xCO + ½CO₂ + ½H₂</td>
<td>(5) 310</td>
</tr>
<tr>
<td></td>
<td>CₓHᵧOᵦ + H₂O → xCO + yH₂</td>
<td>(6)</td>
</tr>
<tr>
<td>Steam reforming</td>
<td>CₓHᵧOᵦ + nH₂O → aCO + (x-a)CO₂ + yH₂</td>
<td>(7) 230</td>
</tr>
<tr>
<td></td>
<td>CₓHᵧOᵦ + (2x-2)H₂O → xCO₂ + (2n+½−z)H₂</td>
<td>(8) 64</td>
</tr>
<tr>
<td>Water gas shift</td>
<td>CO +H₂O → CO₂ + H₂</td>
<td>(9) -41</td>
</tr>
<tr>
<td>Methanation</td>
<td>CO + 3H₂ → CH₄ +H₂O</td>
<td>(10) -206</td>
</tr>
</tbody>
</table>

2.4 Tar formation mechanism and tar removal methods

Tar removal is a major hurdle that hinders the commercialization of biomass gasification.¹ Tar consists of more than 100 different compounds and it produced in a series of complex thermodynamic reactions.⁹ Tar is generally accepted as aromatic hydrocarbons with molecular weight higher than benzene.¹² Milne et al¹³ divides tar into four groups: primary, secondary, alkyl tertiary and condensed tertiary, based on their experimental results obtained from gas phase thermal cracking reactions. Types of tar and their maturation temperature are shown in Table 2.4 and 2.5.

Table 2.4. Types of tar and their chemical compounds¹³,¹⁴
Table 2.5. Tar maturation screen

<table>
<thead>
<tr>
<th>Gasification temperature (K)</th>
<th>Mixed oxygenates</th>
<th>Phenolic ethers</th>
<th>Alkyl phenolic ethers</th>
<th>Heterocyclic ethers</th>
<th>PAH</th>
<th>Large PAH</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>773</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>873</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>973</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1073</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1173</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Many factors can affect the amount and type of tar formed during gasification. These factors include gasifier type and design, operating parameters (temperature, pressure, heating rate and resident time), type of feedstock and type of catalyst used. Tar formation in different type of gasification process and feedstock are shown in Table 2.2. Majority of the gasifiers are operated in a higher temperature range of 700-1000ºC. Generally, higher operating temperatures lead to lower tar content in the product gas. Increasing the pressure of gasifiers also has a positive effect in reducing or eliminating the tar formation. However, it has been observed that increasing the pressure results in greater reduction of light hydrocarbons compared to the heavy hydrocarbons, therefore the fraction of polynuclear aromatic hydrocarbons (PAH) in the tar increases with pressure.

Tar can be removed by 1) physical process, 2) thermal, steam and partial oxidation and 3) catalytic destruction. In the physical process, tar is removed mainly through wet or wet-dry scrubbing. The main problem arising from tar scrubbing that condensed tar components are merely transferred into another (water or solids such as scrubbing lime), which them has to be deposed of in an environmentally acceptable manner. The problem associated with management of these waste water or solids residues. In thermal decomposition, the temperature in excess of 1000ºC is used. Apart from the economics and materials problem, such thermal decomposition can produce a soot that can be even more troublesome for some processes than aromatics. Catalytic steam reforming is the most promising because of their high conversion of tar into syngas.

### 2.5 Catalytic steam reforming of tar from biomass gasification

Several strategies including physical separation (such as filtration and aqueous or liquid scrubbing), thermal cracking, and catalytic tar conversion, have been investigated to remove tar from the product gas. Compared to physical separation and thermal cracking, catalytic tar conversion appears more promising, because it can convert tar into synthesis gas at the same or even lower temperature than the gasification and without the production of wastewater, which will improve the carbon efficiency and entire process efficiency. The catalytic steam reforming of biomass
gasification can be presented by Figure 2.2. In this process, overall steam reforming reaction of biomass can be represented by equation (1) and the most important catalytic

<table>
<thead>
<tr>
<th>Gasifier</th>
<th>Feedstock</th>
<th>Gasifying agent</th>
<th>Operating conditions</th>
<th>Tar content (g/N m³ dry gas)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed bed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Updraft</td>
<td>Straw</td>
<td>Air</td>
<td>400-500</td>
<td>~50.0</td>
<td>15</td>
</tr>
<tr>
<td>Updraft</td>
<td>Sawdust</td>
<td>Air</td>
<td>-</td>
<td>8.6</td>
<td>16</td>
</tr>
<tr>
<td>Updraft</td>
<td>Wood pellet</td>
<td>Air and steam</td>
<td>650</td>
<td>90.3</td>
<td>17</td>
</tr>
<tr>
<td>Updraft</td>
<td>Black pine wood</td>
<td>Air</td>
<td>1000</td>
<td>132.4</td>
<td>18</td>
</tr>
<tr>
<td>Downdraft</td>
<td>Wood chip</td>
<td>Air</td>
<td>-</td>
<td>0.5</td>
<td>19</td>
</tr>
<tr>
<td>Downdraft</td>
<td>Municipal solid</td>
<td>-</td>
<td>-</td>
<td>32.2</td>
<td>18</td>
</tr>
<tr>
<td>Downdraft</td>
<td>Waste</td>
<td>Air</td>
<td>821</td>
<td>2.6-4.0</td>
<td>20</td>
</tr>
<tr>
<td>Downdraft</td>
<td>Black pine wood</td>
<td>Air</td>
<td>1206</td>
<td>1.7-4.0</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>pellet</td>
<td>O₂ and steam</td>
<td>774-934</td>
<td>7.9-16.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hazelnut shell</td>
<td>-</td>
<td>-</td>
<td>7.7-21.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pine wood block</td>
<td>Air</td>
<td>1108</td>
<td>1.2-2.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O₂ and steam</td>
<td>-</td>
<td>-</td>
<td>~101</td>
<td></td>
</tr>
<tr>
<td>Fluidized</td>
<td>Almond shell</td>
<td>Steam</td>
<td>700</td>
<td>6.0-7.0</td>
<td>22</td>
</tr>
<tr>
<td>Bubbling</td>
<td>Pine sawdust</td>
<td>Steam</td>
<td>820</td>
<td>1.0-1.5</td>
<td></td>
</tr>
<tr>
<td>Bubbling</td>
<td>Pine sawdust</td>
<td>Air</td>
<td>790-810</td>
<td>2.0-18.0</td>
<td>23</td>
</tr>
<tr>
<td>Bubbling</td>
<td>Pine sawdust</td>
<td>Steam</td>
<td>750, ~101</td>
<td>180.0</td>
<td>24</td>
</tr>
<tr>
<td>Bubbling</td>
<td>Pine wood</td>
<td>Steam</td>
<td>780, ~101</td>
<td>40.0</td>
<td></td>
</tr>
<tr>
<td>Bubbling</td>
<td>O₂ and steam</td>
<td>750-780, ~101</td>
<td>30.0-80.0</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>Bubbling</td>
<td>Wood</td>
<td>Air</td>
<td>780</td>
<td>~2.0</td>
<td>26</td>
</tr>
<tr>
<td>Bubbling</td>
<td>Shaving/sawdust</td>
<td>Air</td>
<td>857</td>
<td>~0.3</td>
<td></td>
</tr>
<tr>
<td>Bubbling</td>
<td>Rice husk</td>
<td>Air</td>
<td>750</td>
<td>~6.0</td>
<td>27</td>
</tr>
<tr>
<td>Bubbling</td>
<td>Air</td>
<td>701, ~105</td>
<td>15.1</td>
<td></td>
<td>28</td>
</tr>
<tr>
<td>Circulating</td>
<td>Mixed sawdust</td>
<td>Air and steam</td>
<td>815, ~105</td>
<td>0.4</td>
<td>29</td>
</tr>
<tr>
<td>Pressurized</td>
<td>Pine wood sawdust</td>
<td>Air and steam</td>
<td>700-850, 300-1000</td>
<td>5.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.6. Comparison of tar content in product gas of different gasification technologies.
reactions are equation (2)-(4) which can be described as follow:

Overall steam reforming of biomass
\[ C_nH_mO_k + (2n-k)H_2O = nCO_2 + (2n + m/2 - k)H_2 \] \hspace{1cm} \text{equation (1)}

Tars steam reforming
\[ C_nH_m^+ nH_2O \rightarrow nCO + (n + m/2)H_2 \] \hspace{1cm} \text{equation (2)}

Methane steam reforming
\[ CH_4 + H_2O \leftrightarrow CO + 3H_2 \] \hspace{1cm} \text{equation (3)}

Water gas shift
\[ CO + H_2O \leftrightarrow CO_2 + H_2 \] \hspace{1cm} \text{equation (4)}

According to equation (1), the maximum (stoichiometric) yield of hydrogen is \( 2 + m/2n - k/n \) moles per moles of carbon in feed. Equation (2) is irreversible whereas methane steam reforming and water gas shift reaction approach equilibrium. A large molar ratio of steam to hydrocarbon will ensure that the equilibrium for equation (3) and (4) is shifted towards \( H_2 \) production.\textsuperscript{55, 56}

Catalytic tar conversion can proceed in two ways: one approach is incorporating or mixing catalyst with the biomass to achieve so-called catalytic gasification or pyrolysis (primary method), where tar is removed in the gasifier; in the other approach, the gasifier producer gas is treated downstream of the gasifier in a secondary reactor (secondary method), where tar is removed outside the gasifier.\textsuperscript{31}

\textbf{Figure 2.1.} Catalytic steam reforming in decomposition of biomass into synthesis gas.

\subsection*{2.6 Steam reforming using Ni-based catalysts}

The composition of heterogeneous catalysts can be divided into three primary components: (1) an active catalytic phase or metal, (2) a promotor, which increase activity and/or stability, and (3) a high surface area support that facilitates dispersion of the active phase.\textsuperscript{32} A variety of metals have been evaluated for conditioning biomass-derived syngas, and the highest reforming activities were achieved with Ni- and Rh-based catalysts. Nickel-based steam reforming catalysts have been widely used commercially in the petroleum industry for methane and naphtha reforming. These Ni catalysts have also shown activity for tar destruction, hydrocarbon reforming, water-
gas shift (WGS) and NH$_3$ decomposition. Tomishige et al. evaluated Rh, Ru, Pt, Pd, and Ni supported on CeO$_2$-SiO$_2$ for steam reforming of biomass derived tars and they found the order of activity to be Rh > Pt > Ni > Pd > Ru.

Ni catalysts have been reported by many researchers as an effective steam reforming catalyst due to their high performance and low cost. Unfortunately, it has well known that they are easily deactivated by the carbon deposition and sintering of Ni species. Sintering and agglomeration processes occurred because of the high temperature and harsh reaction conditions, which may be present during conditioning of biomass derived syngas. While sintering and agglomeration are of concern, catalyst deactivation by coke formation on catalysts surfaces plays more vital role in the development of tar steam reforming catalysts. Carbon deposition occurs when hydrocarbons first activate on a catalyst surface and then subsequently dissociate. This dissociation leads to surface carbon that can nucleate to form larger carbon deposits and graphitic sheets, which then cover the catalyst surface and block active sites. Coke formation can be adjusted by increasing oxidant (steam and oxygen) concentration, lead to an increased gasification rate and a lower coking rate. The rate of carbon nucleation (i.e., coking) has been investigated along with attempts to slow this process. Theoretical density functional theory (DFT) models have shown that nickel particles size affects the rate of carbon nucleation and particles smaller than a critical size around 25Å do not provide an energetically favorable environment for carbon nucleation to form graphitic sheets. Experimental evidence confirmed this prediction by showing that small nickel particles (<50 Å) did not exhibit graphite formation, and the onset of carbon deposition on small Ni crystallites (7 nm) occurred at 100°C lower temperature than on larger Ni crystallites (100 nm).

2.6.1 Effect of support on Ni-based catalysts

Support material plays an important role in defining the activity and service life of catalyst. Support provide mechanical strength and surfaces on which to disperse the active metal. The activity and basicity, surface area, pore structure, and electronic structure of the support can affect the reducibility, metal dispersion, mechanical strength, and the overall nature of the active sites on a catalyst.

Miyazawa et al. studied steam reforming of biomass tar (SRBT) over Ni catalysts supported on α-Al$_2$O$_3$, ZrO$_2$, TiO$_2$, CeO$_2$ and MgO. They found that Ni/α-Al$_2$O$_3$ had higher activity than the other supported catalysts and the activity order was Ni/α-Al$_2$O$_3$ > Ni/ZrO$_2$ > Ni/TiO$_2$ > Ni/CeO$_2$ > Ni/MgO in terms of residual tar yield. Although Ni/α-Al$_2$O$_3$ showed higher activity, it suffered from a large amount of coke deposition while coke deposition on Ni/CeO$_2$ catalyst was relatively small. This was probably high redox property of CeO$_2$. To improve the performance of Ni/α-Al$_2$O$_3$, Kimura et al. investigated SRBT with Ni/CeO$_2$/α-Al$_2$O$_3$. They found that the Ni/CeO$_2$/α-Al$_2$O$_3$ catalyst prepared by the co-impregnation method exhibited higher performance than Ni/α-Al$_2$O$_3$ and Ni/CeO$_2$/α-Al$_2$O$_3$ prepared by sequential impregnation. CeO$_2$ supplied oxygen atoms to react with the carbonaceous species adsorbed on Ni surface, resulting in high activity and low coke deposition. The catalytic performance of Ni/CeO$_2$/α-Al$_2$O$_3$ catalyst was further improved by the modification with a small amount (~0.1 wt%) of noble metals, reported by Nishikawa et al. The noble metal-promoted
Ni/CeO$_2$/α-Al$_2$O$_3$ catalysts without H$_2$ reduction showed self-activation ability in the steam reforming of tar. Although Al$_2$O$_3$ and metal oxide catalysts are considered as a primary support material for most reforming catalysts, low porosity and low surface area of those catalysts resulted in lower dispersion of metal and large crystallite size.$^{44}$

2.6.2 Ni-based bimetallic catalysts

Addition of the other metals to Ni catalysts can positively affect catalyst activity, reducibility, regenerability, and coke resistance.

Alloying of Ni metal with noble metals has demonstrated an effective approach to improve the catalytic performance. In particularly, the catalyst reducibility and the coverage of oxygen atoms can be controlled by the combination of metals with different oxygen affinity. For example, the combination between Ni and other metal with lower oxygen affinity than Ni can make the alloy reducibility higher than monometallic Ni. In contrasts, the combination between Ni and other metal with higher oxygen affinity than Ni can make coverage of oxygen atoms during the reforming reaction higher than the case of monometallic Ni catalyst.$^{31}$ Wang et al. reported$^{46}$ that the addition of suitable amount of Fe to Ni/α-Al$_2$O$_3$ enhanced the catalytic performance of the steam reforming of tar. The highest activity was obtained on Ni-Fe/α-Al$_2$O$_3$ (Fe/Ni = 0.5), which exhibited higher activity, stability, and resistance to coke deposition than the corresponding monometallic Ni/α-Al$_2$O$_3$ and Fe/α-Al$_2$O$_3$ catalysts. High performance of the Ni-Fe/α-Al$_2$O$_3$ catalyst was attributed to the synergy between the activation of tar on the Ni species and the supply of oxygen atoms from neighboring Fe sites.

The promoting effect of alloying was also observed on Ni-Co/α-Al$_2$O$_3$. For Ni-Co/α-Al$_2$O$_3$ catalyst, (Wang et al.$^{47}$), the optimum composition was obtained at Co/Ni =0.25. Similarly to Ni-Fe/α-Al$_2$O$_3$, Ni-Co/α-Al$_2$O$_3$ catalyst showed the formation of Ni-Co alloys and gave higher activity, stability and resistance to coke deposition than the corresponding monometallic Ni/α-Al$_2$O$_3$ and Co/α-Al$_2$O$_3$ catalysts.

Bimetallic catalysts containing manganese oxide have been widely applied in many reactions, including steam reforming.$^{57,58}$ owing to its excellent redox property. Koike et al.$^{57}$ studied Ni-Mn/Al$_2$O$_3$ catalyst and suggested that improvements in performance in CSRT-biomass were due to the supply of oxygen atoms from MnO$_x$ to Ni species to enhance the reaction between carbonaceous and oxygen on the Ni surface. Lee et al.$^{59}$ examined steam reforming of ethanol with Mn/Co$_{10}$Si$_{90}$MCM-48 catalyst and discussed that MnO$_x$ provided oxygen to Co metal to increase hydrogen production.

2.6.3 Mesoporous silica SBA-15 supported Ni catalyst

Mesoporous materials are ones of the most promissory catalyst support, ensuring an adequate dispersion of catalytic metal owing to its high surface area, generating metallic clusters of small size, smaller diameter, homogeneous distribution and good structural regularity.$^{44}$

Kim et al.$^{48}$ studied ethanol steam reforming (ESR) reaction over SBA-15 supported Ni-W catalysts. the catalytic performance of Ni-W/SBA-15 was improved relative to Ni/SBA-15, and the catalytic deactivation was rather retarded during ESR. H$_2$ production of about 80% was maintained at 600°C until 80 h without any catalytic deactivation over Ni$_{0.95}$W$_{0.05}$/SBA-15 catalyst. They proposed ESR model in which an ethanol molecules over the Ni sites is transformed to CH$_4$ and CO over the NiW/SBA-
15 catalyst, which resulted in highly concentrated H\textsubscript{2} evaluation through CH\textsubscript{4}-SR over Ni or NiO, while CO-WGS was performed over NiW alloy of the NiW/SBA-15 catalysts. The introduction W oxide to Ni/SBA-15 catalyst had favorable effect on high hydrogen production, and also reduced catalyst deactivation by decreasing sintering phenome between Ni particles.

Catalytic steam reforming of biomass tar (SRBT) with highly dispersed SBA-15 supported Ni-Fe bimetallic catalysts was studied by Kathiraser et al.\textsuperscript{49}. The catalysts were prepared by the oleic acid assisted incipient wetness impregnation method and the resultant metal particle sizes of catalysts were smaller than 3 nm. An optimum catalyst composition of 6Ni-1Fe/SBA-15 gave superior catalyst performance in term of activity and stability. They found that addition of Fe is effective in suppressing the carbon deposition rate by up to 2.5 times due to oxygen scavenging effect of Fe (owing to it redox properties), which can effectively promote carbon gasification whilst providing sufficient active metal sites exposure for improved gasification activity.

Zhao et al.\textsuperscript{50} examined hydrogen production from cellulose decomposition over Ni-Co/SBA-15 catalysts. They studied the activity of catalysts with different Ni and Co ratio: 1:1(NiCo), 2:1(Ni\textsubscript{2}Co) and 1:2 (NiCo\textsubscript{2}) and observed that 10wt%NiCo\textsubscript{2}/SBA-15 was the most active bimetallic catalyst, yielding 259 ml H\textsubscript{2}/g cellulose without water addition in the cellulose decomposition process. Addition of water further enhanced H\textsubscript{2} yield to 405 ml/g cellulose.

References

52. NETL (National Energy Technology Laboratory), https://www.netl.doe.gov/research/coal/energy systems/gasification.
CHAPTER 3
EXPERIMENTAL METHODS

3.1 Introduction
Chapter 3 includes the method and procedures for preparation of the SBA-15 supports and supported metal catalysts, method and procedure for characterization of catalyst, and the experimental procedure and experimental set up of the catalytic steam reforming of biomass gasification tar process (CSRT-biomass).

3.2 Synthesis of mesoporous SBA-15 materials
Mesoporous SBA-15 support with different pore size were synthesized using the methods reported by D. Zhao et al. and M. Kruk et al.\textsuperscript{1,3}

3.2.1 Synthesis of SBA-15 with regular pore size
Mesoporous SBA-15 with regular pore size (pore size; 4.5 - 5 nm) was prepared by soft template procedure using surfactant (triblock copolymer Pluronic P123; PEO20PPO70PEO20). The molar ratio of synthesis mixture was P123:TEOS:HCl:H\textsubscript{2}O=1:0.00278:0.966:24.02. In this synthesis, 4 g of P123 was dissolved in 25 g of HCl (conc. 35%) solution and stirred at room temperature until the solution become clear. Subsequently, 8.54 g *tetraethyl orthosilicate* (TEOS) was added and the mixture was stirred at 313 K for 24 h. Then, the product was aged in an oven at 363 K for 20 h. The resulting as-synthesized product was isolated by filtration and washing with water and dried at 343 K overnight. Finally, the solid powder was calcined in air to remove the templates at 823 K with a heating rate of 1 K/min for 4 h and the white SBA-15 powders were obtained.

3.2.2 Synthesis of SBA-15 with larger pore size
Mesoporous SBA-15 with larger pore size (5-12nm) as also prepared using P123 surfactant, and Hexane as micelle expander. The molar composition used in this synthesis was P123:TEOS:C\textsubscript{6}H\textsubscript{14}:NH\textsubscript{4}F:HCl:H\textsubscript{2}O 1:0.0168:4.02:0.295:4.42:133. The synthesis procedure was the same above but the different reaction condition was used. 8.145 g P123 and 0.0918 g NH\textsubscript{4}F was dissolved in 38.67 g HCl (conc. 35%) solution and stirred at room temperature. Then, the solution was transferred to a water batch set at 288±1 K and stirred for 1 h using mechanical stirrer. A mixture of 17.08 g of TEOS and 43.76 ml of hexane was added and continued stirring at 288 K for 24 h. Then, in order to access the effect of aging temperature and time on the formation of mesopore size and structure, aging were performed at 333 K or 353 for 48 h, 120 h or 72 h. The product was collected by centrifugation and washing with water and dried in an oven at 343 K overnight. Large pore SBA-15 was obtained after calcination in air at 773 K with a heating rate of 1 K/min for 6 h.
3.3 Synthesis of the supported catalysts

The supported Ni, Co and Fe catalysts were synthesized by precipitation method and Ni-MnOₓ/SBA-15 catalysts were synthesized by EG-assisted impregnation procedure.

3.3.1 Precipitation method

The supported transition metal (Ni, Co and Fe) catalysts were synthesized by the precipitation method. Commercial SiO₂ and regular pore-SBA-15 materials (avg. pore size: 4.8 nm) are used as a support. Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, and Fe(NO₃)₃·9H₂O are used as the metal precursors. In the 10wt% NiO/SiO₂ (represent as wt% Ni) catalyst preparation, 4.955 g of Ni(NO₃)₂·6H₂O in 200 ml distilled water solution was mixed with 9 g of the supports, SBA-15 or SiO₂ (Ultrasonic agitation was conducted for 30 min when SBA-15 was used as support in order to release air inside of the pores of SBA-15). The slurry was slowly added in drops into a beaker containing Na₂CO₃ solution (2.708 g in 200 ml distilled water) under stirring at room temperature and a constant pH of 10±5, where the pH of solution was adjusted with NaOH aq (2M). The resulting suspension was kept at room temperature for 24 h. The obtained precipitate was centrifuged under 11000 rpm for 10 min and washed with distilled water. This cycle continued until to be pH 7. The catalytic precursor was dried at 358 K overnight. The supported metal catalyst was obtained after calcination at 723 K for 4 h.

SiO₂ supported Co and Fe catalysts, different metal loaded SiO₂ and SBA-15 supported Ni catalysts were also prepared with the same procedure above. The prepared catalysts were denoted as 10Ni/SiO₂, 10Co/SiO₂, 10Fe/SiO₂, 20Ni/SiO₂, 30Ni/SiO₂, 10Ni/SBA-15, 20Ni/SBA-15 and 30Ni/SBA-15.

3.3.2 EG-assisted impregnation method

Ethylene glycol (EG) assisted impregnation procedure was used in synthesis of the large pore-SBA-15 supported Ni, Mn and Ni-Mn catalysts. During impregnation, the EG additive in metal nitrate aqueous solution could deliver and package the metal species into the channel of mesoporous SBA-15 and also resulted in high dispersion Ni metal species and small particle size. The metal loading was set 10 wt % (represented as wt% Ni and/or wt% Mn) of all catalysts. The molar ratio of metal species to EG was fixed to 10. In a typical catalyst preparation of Ni/SBA-15 catalyst, EG (4.652 g) and Ni(NO₃)₂·6H₂O (2.178 g) dissolved in ultra-pure water (120 ml) and mixed with SBA-15 support (4 g) material. The resultant slurry was pre-stirred under a magnetic stirrer for 12 h. The mixture was impregnated at 353 K in a water bath with intermittent stirring and kept at this temperature until all the water was evaporated. The catalyst precursor powder was then dried at 373 K in an oven overnight and calcined at 723 K or 973 for 2 h in a furnace. 10Mn/SBA-15 and Ni-MnOₓ/SBA-15 catalysts are also prepared with the same procedure. The prepared catalysts are denoted and listed in Table 3.1 as follow.

| Table 3.1. List of catalysts prepared by EG-assisted impregnation technique |
|-------------------------------|-------------------------------|
| Catalysts                     | Calcination temperature (K)   |
| 10Ni/SiO₂                     | 723                           |
| 10Co/SiO₂                     | 723                           |
| 10Fe/SiO₂                     | 723                           |
| 20Ni/SiO₂                     | 723                           |
| 30Ni/SiO₂                     | 723                           |
| 10Ni/SBA-15                   | 723                           |
| 20Ni/SBA-15                   | 723                           |
| 30Ni/SBA-15                   | 723                           |
| 10Mn/SBA-15                   | 973                           |
| Ni-MnOₓ/SBA-15                | 973                           |
3.4 Characterization of catalysts

3.4.1 N\(_2\)-physisorption

The specific surface area is one of the essential physical properties of the supported metal catalysts involved in heterogeneous reactions. The surface area of support material is important parameter to disperse the active metal species onto it surface. Apart from surface area, N\(_2\) adsorption-desorption measurement can also provide the pore size distribution and pore geometry. A standardized procedure for determining the internal surface area of a porous material is based on the adsorption of N\(_2\) at liquid N\(_2\) temperature onto the internal surfaces of the carrier. Each adsorbed N\(_2\) molecule occupies an area of the surface comparable to its cross-sectional area (16.2Å\(^2\)). By measuring the number of N\(_2\) molecules adsorbed at monolayer coverage, one can calculate the internal surface area.

The specific surface area, pore diameter and pore volume of the supports and the supported catalysts were measured using a Micromeritics Tristar 3000 by N\(_2\) adsorption at 77 K. The sample (0.8 -1.5 g) was degassed under vacuum at 200°C for 6 h before measurement. The N\(_2\) adsorption–desorption isotherms was measured in 10\(^{-6}\) –1 relative pressure ranges. The specific surface area was determined by Brunauer-Emmett-Teller (BET) method.

\[
\frac{P}{V(P_0 - P)} = \frac{1}{CV_m} + \frac{C - 1}{CV_m} \cdot \frac{P}{P_0}
\]

Where, \(C\) = constant

\(V_m\) = monolayer adsorption amount

\(V\) = adsorbed amount at the equilibrium pressure P

This theory well fits to type II and IV isotherms at the relative pressure between 0.05 and 0.35. The monolayer adsorption amount (\(V_m\)) and \(C\) parameter are calculated from the slope and intercept of BET-plot by using the least square fitting. \(C\) parameter represents the surface interaction energy, so it must take a positive value.

The specific surface area is calculated from this \(V_m\) and cross sectional area of an adsorbed molecules (\(\sigma\)).

\[
S_{BET} = V_m \times N_A \times \sigma
\]

Where,

\(N_A\) = Avogadro constant

\(\sigma\) = cross sectional area of N\(_2\) molecule

Total pore volume pore size were calculated respectively by Barrett-Joyner-Halenda (BJH) methods. At saturation (\(P/P_0 \approx 1\)) the liquid volume of different adsorbates, when measured on porous adsorbents, is essentially constant and is independent of adsorbate. This constancy of adsorbed liquid at saturation provides direct evidence that the pores are filled. The amount of adsorption can be used to calculate total pore volume, it can be calculated from weight of N\(_2\) adsorbed at \(P/P_0 =0.99\) by using the following equation.

\[
V_p = \frac{W}{\rho}
\]

Where, \(V_p\) = total pore volume
W = gram of N\textsubscript{2} are adsorbed
\( \rho \) = density of liquid

Surface area and pore volume can be represented by the below equations;

\[ V_p = \Pi r_p^2 L \text{ and } S_{BET} = 2\Pi r_p L \]

And pore radius \((r_p)\) and pore size \((D_p)\) were calculated as below.

\[ r_p = \frac{2V_p}{S_{BET}} \quad \text{and} \quad D_p = 2r_p \]

3.4.2 X-ray diffraction (XRD) analysis

Small-angle XRD measurement is used to access the pore structure of SBA-15 material and SBA-15 supported catalysts. The samples were scanned at the region of \(2\theta = 0.5-5^\circ\) with a scanning rate of 0.3 \(^\circ\)/min. XRD diffraction signal was accessed using SmartLab, Rigaku, with Cu K\textalpha\ radiation (wavelength = 1.5418 Å). The interplaner distances or plane distances of the hexagonal porous structure of the catalysts were calculated by Bragg’s law.

\[ n\lambda = 2d\sin\theta \]

Where,
- \( n = \) positive integer
- \( \lambda = \) wavelength of incident light
- \( d = \) plane distance

Wide-angle XRD measurement is used to determine the crystallite structure and crystallite size of the supported metal catalysts. The X-ray diffraction patterns of the catalysts were accessed using Miniflex 600, Rigaku with Cu K\textalpha\ radiation (wavelength = 1.5418 Å). The scanning range of the sample was set 10-80\(^\circ\) in 2\(\theta\) with a scanning rate of 2\(^\circ\)/min. The crystallite size was calculated by Scherrer’s equation:

\[ d = \frac{0.95 \lambda}{(\beta - \beta_o)\cos\theta} \]

Where, \((\beta - \beta_o)\) = full width at half maximum intensity of the peak
- \(d = \) the crystallite size

3.4.3 Transmission electron microscopy (TEM) observation

TEM is a vital characterization tool directly imaging nanomaterial to obtain quantitative measures of particle and/or grain size, size distribution and morphology. TEM images the transmission of a focused beam of electrons through a sample, forming an image in an analogous way to a light microscope. TEM imaging has significantly higher resolution (by a factor of about 1000!) than light based imaging techniques. Successful imaging of nanoparticles using TEM depends on the contrast of sample relative to the background.

TEM images of the catalysts were taken by JEOL, JEM-2010. The sample solution was prepared by suspending in ethanol and dispersing it by sonication. A drop of solution was placed onto the copper-grid coated with a thin carbon film and allowed to
dry, typically under vacuum, prior to TEM observation.

3.4.4 Temperature program reduction (TPR)

The degree of catalyst reduction is one of the important factor affecting the catalyst activity. TPR measurement can represent to determine the metal reducibility, dispersion and location of metal species, metal-support interaction and reduction temperature of the catalysts.

TPR experiments were performed on a quadrupole mass spectrometry (MKS EVP-220-001). Before reduction experiment, the catalyst (0.3 g) was dried under 30ml/min Ar flow while increasing the temperature from room temperature to 120ºC with a constant increase rate of 15ºC/min and holding at this temperature for 1 h. Then, TPR experiment was conducted using 10 vol% H2 in 30ml/min Ar flow and a temperature range from 298ºC to 1173ºC at a rate of 10ºC/min. The analytical area profile was recorded by mass spectroscopy.

3.4.5 Temperature program oxidation (TPO)

In the catalytic steam reforming of biomass derived-tar reaction, carbon deposition on the catalyst surface was occurred and the amount of deposited carbon (coke) was measured by TPO.

TPO were performed in the same equipment with TPR. In TPO measurement, the catalyst (0.2 g) was dried under 30ml/min Ar flow while increasing the temperature from room temperature to 120ºC with a constant increase rate of 15ºC/min and holding at this temperature for 1 h. Then, TPR profile was recorded from 298 K to 1173 K at a heating rate of 10 K/min under 3 vol% O2 in 30ml/min Ar flow. The amount of O2, CO, CO2, H2 and H2O in the exhaust gas was continuously monitored by QMS (MKS EVP-220-001).

3.5 Thermal decomposition and steam reforming of biomass gasification experiments

Thermal decomposition of biomass is a biomass gasification process. In this process, biomass is heated to the desired temperature to decomposition of gas fraction, char fraction, and tar fraction in the absence of air or oxygen. In the steam reforming of biomass, water is supplied during the biomass gasification process. These process were studied in a single-stage fixed-bed reactor system.

In this process, 0.5 g of biomass was fixed in the reactor and heating up the reactor to 873 K or 973 K with a heating rate of 25 K/min and hold at this temperature for 2 h. The reaction was performed under the 50 mL/min of N2 carrier gas flow. In steam reforming process, water was injected into the reaction system by using micro feeder with a feeding rate of 80 mg/min. The evolved gas was collected by plastic bags after passing through the cold trap. The product gases were analyzed by the gas chromatographs (GC) equipped with the thermal conductivity detectors (TCD). H2 composition in gas mixture was detected using the GC with Ar as carrier gas, and the composition of CO, CH4 and CO2 were analyzed by the GC with He carrier gas. The operating conditions for GC analysis are described in article 3.7 and the experimental system for single-stage fixed-bed reactor is shown in Figure 3.1.
The carbon content and chemical formation of sawdust were assumed as 43 wt% and C_6H_{10}O_5. Therefore, 0.215 g of carbon is contained in 0.5 g of sawdust (m_{C,BM}). In the catalytic steam reforming process of biomass tar, carbon deposition on the catalyst surface was usually occurred and the product fractions were gas, char and tar. Assuming that carbon deposition was not occurred on the catalyst surface during the activity test. Therefore, carbon-based product yield (Y_C) can be written as shown below:

\[
Y_C = \left(\frac{m_{C,GAS} + m_{C,CHAR} + m_{C,TAR}}{m_{C,BM}}\right) \times 100
\]  

(1)

\[
m_{C,BM} = m_{C,GAS} + m_{C,CHAR} + m_{C,TAR}
\]  

(2)

Where, \(m_{C,BM}\) is mass of carbon in sawdust, \(m_{C,GAS}\) (g) is mass of carbon in CO+CO_2+CH_4 of product gas, \(m_{C,CHAR}\) (g) is mass of carbon remained after the activity test, and \(m_{C,TAR}\) (g) is calculated from equation (1).

Overall steam reofrming of cellulose in biomass can be represent as equation (3).

\[
C_6H_{10}O_5 + 7H_2O \rightarrow 6CO_2 + 12H_2
\]  

(3)
Thus, maximum stoichiometry yield of \( H_2 \) is 2 moles/mole of carbon in feed. Yields of product gas (CO, CH\(_4\), CO\(_2\) and \( H_2 \)) were calculated by using equation (4) and (5).

\[
Y_{CO/CH4/CO2} = \left( \text{mass of C in CO, CO}_2, \ CH_4 / m_{C,BM} \right) \times 100 \quad (4)
\]

\[
Y_{H2} = \left( \text{mol of H}_2 / \text{maximum stoichiometric yield of H}_2 \right) \times 100 \quad (5)
\]

### 3.6 Catalytic steam reforming experiment

The performances of the catalysts were investigated in a two-stage fixed-bed reactor.

#### 3.6.1 Activity test with a single-stage fixed-bed reactor

The catalytic steam reforming of sawdust was evaluated in a single-stage fixed-bed reactor (ID = 8 mm × L = 500 mm). The catalyst and biomass were fixed in a one single-bed. For each experiment, 0.5 g of catalyst was placed into the reactor and reduction of catalyst was performed using 30 mL/min \( H_2 \) gas at 773 K for 1 h before the activity test. After reduction, the reactor was cold down to room temperature. After that, 0.5 g of sawdust was put on the catalyst bed, and the catalyst and sawdust were separated with a layer of quartz wool. In the catalytic activity test, the reactor was heating up to 873 K with a heating rate of 25 K/min and hold at this temperature for 2 h. The reaction was performed under the 50 mL/min of \( N_2 \) carrier gas flow. Water was injected into the reaction system by using micro feeder with a feeding rate of 80 mg/min. The other operating parameters and calculation for carbon based yield are same as described in article 3.5.

#### 3.6.2 Activity test in a two-stage fixed-bed reactor

The catalytic steam reforming of biomass tar was usually operate in a temperature range of 873-1073 K due to endothermic nature of the reforming reaction. In the pyrolysis of biomass, decomposition of biomass started at 250-300ºC and the highest rate of volatile matters (tar compounds) formation was occurred at 350-400ºC. In this temperature range, catalysts are not active enough that it cannot perform tar conversion effectively and shows low tar reforming activity. Therefore, it can be suggested that even an excellent tar reforming catalyst cannot exhibit high tar reforming activity by using a single-stage fixed-bed reactor system in CSRT-biomass process. To solve this problem, a two-stage fixed-bed reactor system was considered and used in the next experiments.
The pyrolysis-catalytic steam reforming experiment was conducted in a two-stage fixed-bed quartz reactor. Two electrical furnaces were used to separately control the temperature of each bed. Experimental setup is described in Figure 3.3. The upper stage was fixed pyrolysis bed in which 0.5 g of sawdust was loaded and the lower stage was fixed catalyst bed in which 0.5 g of catalyst was loaded. The catalyst was pre-reduced with an H₂/N₂ (30/30 ml/min) mixed gas at 773 K or 973 K for 1 h. In the activity test, pyrolysis of sawdust was carried out by heating up the pyrolysis bed to 973 K within 15 min and holding at this temperature for 1 h. At the same time, catalytic steam reforming of volatile matters (mainly tar), products of pyrolysis, took place in the catalyst bed which was maintained at 773 K. The experiment was performed under the 50 ml/min of N₂ carrier flow. 80 mg/min of water was supplied with a micro-feeder. The gas compositions were analyzed by the gas chromatographs (GC).

Caron-based mass balance can be written by equation (1) and carbon-based yield (Y_C) of the products (gas, char, tar and coke) was calculated by equation (2);

\[ m_{C,BM} = m_{C,GAS} + m_{C,CHAR} + m_{C,COKE} + m_{C,TAR} \]  

(1)
\[ Y_C = \left( \frac{m_{C,GAS} + m_{C,CHAR} + m_{C,TAR}}{m_{C,BM}} \right) \times 100 \] (2)

Where \( A \) is \( m_{C,GAS} \) or \( m_{C,CHAR} \) or \( m_{C,COKE} \) or \( m_{C,TAR} \) and \( B \) is the mass of carbon in biomass \( (m_{C,BM}) \). \( m_{C,GAS} \) is the mass of carbon in product gases \( (CO+CO_2+CH_4) \) obtained from experiments, \( m_{C,CHAR} \) is the mass of carbon that remains as a char after the activity test, \( m_{C,COKE} \) is obtained from TPO measurement of the deposited carbon on the used catalyst, and \( m_{C,TAR} \) is the mass of carbon in tar and calculated using equation (2). The composition of the sawdust (wt% dry basis) used in this experiment was \( C = 48.39\% \), \( H = 5.9\% \), \( N = 0.11 \% \) and \( O = 45.6\% \). Therefore, chemical formular of biomass can be written as \( C_6H_9O_4 \).

Overall steam reofrming of cellulose in biomss can be represent as equation (3).

\[ C_6H_9O_4 + 8H_2O \rightarrow 6CO_2 + 25/2 \text{H}_2 \] (3)

Thus, maximum stoichiometry yield of \( \text{H}_2 \) is 2.083 moles/mole of carbon in feed. Yields of product gas \( (CO, CH_4, CO_2 \text{ and } \text{H}_2) \) were calculated by using equation (4) and (5).
\[ Y_{\text{CO/CH4/CO2}} = \left( \frac{\text{mass of C in CO, CO}_2, \text{CH}_4}{m_{\text{BM}}} \right) \times 100 \]  \hspace{1cm} (4)

\[ Y_{\text{H2}} = \left( \frac{\text{mol of H2}}{\text{maximum stoichiometric yield of H2}} \right) \times 100 \]  \hspace{1cm} (5)

3.7 Gas chromatographic (GC) analysis

The product gasses were analyzed by the gas chromatography (GC), Shimazu 8A, equipped with activated carbon columns and TCD detectors. The GC using Ar as carrier gas was used to detect the H\(_2\) gas while the composition of CO, CH\(_4\) and CO\(_2\) in product gas were detected by GC using He carrier gas. The operation conditions of the GC are as follows.

1) GC for H\(_2\) detection
   - Column temperature: 90\(^\circ\)C
   - Detector temperature: 130\(^\circ\)C

2) GC for CO, CH\(_4\) and CO\(_2\) detection
   - Column temperature: 100\(^\circ\)C
   - Detector temperature: 140\(^\circ\)C

References
CHAPTER 4

STEAM-REFORMING PROCESS OF BIOMASS OVER TRANSITION METAL CATALYSTS

4.1 Introduction

Biomass is a renewable energy resource and it can either be used directly via combustion to produce heat, or indirectly after converting it to various forms of biofuels. The main routes of producing fuels from biomass include (1) gasification to produce syngas, (2) liquefaction and pyrolysis to produce bio-oils, (3) hydrolysis to form aqueous sugars or lignin, which can be further processed via fermentation or reforming, and (4) transesterification of triglycerides to produce biodiesel. Among these processes biomass gasification had attracted much attention from both industrial and academic researchers due to its high conversion efficiency of biomass into fuels.

One of the primary obstacles to commercializing this technology is the formation of tars during biomass gasification. Tars can cause several operational problems, thus blocking, fouling, corrosion, erosion, and abrasion of process equipment such as engines and turbines. In addition, large amounts of wastewater produce from scrubbing processes that require downstream treatment and/or recycle.

Catalytic steam reforming systems are more efficient than the other tar-removing processes because they can eliminate almost all of tars and also improve carbon efficiency by reforming tars to more synthesis gas. Biomass derived tar steam reforming have been evaluated with a variety of metals that the results came out Rh, Ni, and Pt were the best potential metals due to their high catalytic activity.

The high price of Rh and Pt limits for the industrial application that most of the studies have focused on low material cost Ni-based catalysts. However, Ni catalysts suffer from coke deposition, leading to deactivation of the catalyst.

Addition of promoter (other metals) can generally improve catalytic activity and resistance to coke deposition. Development of promoted catalysts has been conducted by many studies. Co catalysts have reported as effective catalyst for the steam gasification of biomass, partial oxidation of methane, and steam reforming of ethanol. Addition of suitable amount of Fe to Ni/Al₂O₃ catalyst enhanced the catalytic performance in the steam reforming of tar.

Supports material can provide mechanical strength, surface on which to disperse active catalytic materials and they may also play a chemical role in catalysis. Mesoporous materials have attracted substantial interest for their use as catalyst-immobilization matrices. These features include high surface area, chemical, thermal, and mechanical stability, highly uniform pore distribution and pore size, high adsorption capacity, and an ordered porous network for free diffusion of substrates and reaction products.

In this study, SiO₂ and SBA-15 supported Ni, Fe, Co, and Ni-Co catalysts were synthesized and the activity tests were performed in the biomass derived tar steam reforming reaction.
4.2 Experimental

4.2.1 Preparation of SBA-15 material

The SBA-15 with regular pore size (4 - 5 nm) was prepared by a soft template procedure as described in article 3.2.1.

4.2.2 Preparation of catalysts

The SiO₂ supported Ni, Co and Fe catalysts, and SBA-15 supported Ni catalysts were synthesized by the precipitation procedure as described in article 3.3.1.

4.2.3 Characterization of catalysts

The specific surface area, pore size, and pore volume of the catalysts were obtained by N₂-physisorption measurement. The XRD profiles of the catalysts were taken by Cu Kα radiation.

4.2.4 Thermal decomposition and steam reforming experiment

The thermal decomposition of biomass, and steam reforming and catalytic steam reforming of biomass derived-tar were evaluated in a single-stage fixed-bed reactor as described in article 3.5.1.

4.3 Results and Discussion

4.3.1 Gasification of biomass by thermal decomposition, steam reforming and catalytic steam reforming

Gasification of biomass into synthesis gas was studied by the thermal decomposition, steam reforming and catalytic steam reforming process. The reaction were conducted at 873 K. H₂ yield % and selectivity of carbon product (gas, char, and tar) are reported in Figure 4.1. The production rate of product as a function of reaction time was described in Figure A1.

The yields of gas, char and tar from gasification of biomass at 873 K can be seen Figure 4.1 (A). In the thermal decomposition and steam reforming process, formation rates of product gas were almost the same. However, the gas formation rate was increased in the catalytic steam reforming process. Catalytic steam reforming enhanced gas formation rate to 1.6 times using SBA-15 material and 4.7 times using 10Ni/SBA-15 catalyst compared to steam reforming without catalyst process, indicates significant role of catalyst in steam reforming of biomass gasification process. Char yield was decreased by steam reforming and catalytic steam reforming. Therefore, it can be suggested char steam reforming reaction was occurred by these process. In the result of tar yields, no significant different was observed in thermal decomposition, steam reforming and catalytic steam reforming with SBA-15 material, indicate steam and SBA-15 material cannot support to occur tar decomposition reaction. In using 10Ni/SBA-15 catalyst, tar yield was decreased by tar steam reforming reaction on the Ni metal surface.

Addition of steam and catalyst to the biomass decomposition process showed significant enhancement in H₂ gas formation amount (Figure 4.1(B)). In thermal decomposition, H₂ formation amount was low and it was 0.63 mmol/g of biomass. Improvement in H₂ formation amounts were 3.5 times by steam reforming, 5.7 times in
steam reforming with SBA-15 and 23.2 times in steam reforming with 10Ni/SBA-15 catalyst.

![Graph](image)

**Figure 4.1.** (A) Carbon selectivity and (B) H$_2$ yield of biomass decomposition process at the reaction temperature of 873 K.

4.3.2 Catalytic steam reforming using transition metal Co/SiO$_2$, Fe/SiO$_2$ and Ni/SiO$_2$ catalysts

The biomass gasification produces gases (H$_2$, CO, CH$_4$ and CO$_2$), solids (char), and liquids (tar). The purpose of gasification is to convert biomass to the synthesis gas. So, the catalytic steam reforming reaction with the high conversion of char and tar to the product gas is always desired. The yield of the carbon products (gas, char and tar), and H$_2$ of the catalysts are shown in Figure 4.2. The production rate of product as a function of reaction time was described in Figure A2.

In Figure 4.2(A), it can be seen that the steam reforming experiment without catalyst resulted high in tar formation. The tar formations were reduced by using catalysts. Ni/SiO$_2$ catalysts showed lower residual tar % than Co/SiO$_2$ and Fe/SiO$_2$ catalysts, resulting in higher gas formation rate and H$_2$ formation. In the catalytic tar
reforming, it can be explained that the hydrocarbons, CO, CH₄, and CO₂ from the pyrolysis of sawdust simultaneously reacted with steam over the catalyst surface to produce more H₂ and synthesis gases. Therefore, gas formation rate is mainly depend on tar conversion. The catalytic tar reforming improved gas formation to 2 - 4 times and H₂ gas formation to 2 - 4.2 time depending on the different metal catalysts. Char amounts were nearly the same for all catalysts and lower percentage than without catalyst experiment. Therefore, some extend of conversion of char to gas was occurred by char steam reforming reaction.

![Graph A](image1)

**Figure 4.2. (A)** Carbon selectivity and (B) H₂ yield of SiO₂ supported 10wt% transition metal catalysts; reaction temperature 873 K.

Among Co, Fe and Ni metal catalysts, Ni metal showed higher tar conversion and H₂ yield than Co and Fe catalysts that more study was continued using Ni catalysts.

4.3.3 Effect of metal loading and support material in Ni catalysts
The effect of metal loading and support was investigated with 10-30wt% Ni/SiO₂,
and 10-30% Ni/SBA-15 catalysts. Figure 4.3(A) and (B) shows carbon selectivity and H\textsubscript{2} yield in the catalytic steam reforming with the different metal loading of Ni/SiO\textsubscript{2} and Ni/SBA-15 catalysts. The production rate of product as a function of reaction time was described in Figure A3.

![Diagram of carbon selectivity and H\textsubscript{2} yield](image)

Figure 4.3. (A) Carbon selectivity and (B) H\textsubscript{2} yield of SiO\textsubscript{2} and SBA-15 supported 10wt%, 20wt% and 30wt% Ni catalysts; reaction temperature 873 K.

In the study of metal loading, the performance of the Ni/SiO\textsubscript{2} and Ni/SBA-15 catalysts were improved by increasing metal loading from 10% to 20%. H\textsubscript{2} yield showed almost the same as in 20wt% and 30wt% metal loaded catalysts. In the 30wt%Ni catalysts, it can be suggested that the aggregation of metal particles led to larger particle size and decrease in available of active surface metal species. This indicated volcano-type dependent of catalytic steam reforming reaction.

The Ni/SBA-15 catalysts exhibited the higher H\textsubscript{2} yield and C\textsubscript{GAS} formation than that of the Ni/SiO\textsubscript{2} catalysts. These results implied that dispersion of Ni nanoparticle enhanced on the SBA-15 surface rather than SiO\textsubscript{2} due to larger surface area of SBA-15.

According to the above explanation, it was suggested that the 20Ni/SBA-15 was
the most suitable steam reforming catalyst with H₂ formation of 17 mmol, and X_TAR of 73%.

4.3.4 Characteristics of the fresh catalysts
The N₂ adsorption-desorption isotherm of SiO₂ supported transition metal catalysts and SiO₂ material, and SBA-15 supported Ni catalysts and SBA-15 materials are showed in Figure 4.4 (A) and (B). Pore size distribution of SiO₂, SBA-15 and supported catalysts are described in Figure 4.5. Surface structural properties (surface area, pore volume and pore size) of the fresh catalysts are summarized in Table 4.1.

![Figure 4.4](image-url)

**Figure 4.4.** N₂ adsorption-desorption isotherms (A) SiO₂ and SiO₂ supported catalysts (B) SBA-15 and SBA-15 supported catalysts.

In Figure 4.4 (A), it can be seen that SiO₂ material showed type IV isotherm with H₄ hysteresis loop. It is the nature of narrow slit like pores, particles with internal voids of irregular shape and broad size distribution, hollow spheres with walls composed of ordered mesoporous silica. It has wide range of pore size distribution (~1-80 nm) with
large amount of microspores. The nitrogen adsorption/desorption of SBA-15 (Figure 4.4 (B)) was typical type IV isotherm with H1 hysteresis loops, indicating relatively high pore size uniformity and facile pore connectivity. This is the characteristic for

### Table 4.1. Structural properties of the fresh catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>BET surface area(m²/g)</th>
<th>Total Pore volume(cm³/g)</th>
<th>Avg. pore size(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10Co/SiO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10Fe/SiO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20Ni/SiO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30Ni/SiO₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBA-15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10Ni/SBA-15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20Ni/SBA-15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30Ni/SBA-15</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

**Figure 4.5.** Pore size distribution of (A) SiO₂ and SiO₂ supported catalysts (B) SBA-15 and SBA-15 supported catalysts.
mesoporous materials according to IUCP classification. The isotherms of supported metal catalysts showed deformation of hysteresis loop of SiO$_2$ or SBA-15 supports and the catalysts have random pore size distribution. Pore size distribution of SBA-15 was narrow and maximize at around 6 nm. High surface area and large pore volume with uniform pore size were additional advantage of SBA-15 material.

Figure 4.6 represents for XRD patterns of the fresh catalysts.

<table>
<thead>
<tr>
<th></th>
<th>2 Theta (deg)</th>
<th>Intensity (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10Co/SiO$_2$</td>
<td>0.75</td>
<td>12.1</td>
</tr>
<tr>
<td>10Fe/SiO$_2$</td>
<td>0.68</td>
<td>12.4</td>
</tr>
<tr>
<td>10Ni/SiO$_2$</td>
<td>0.80</td>
<td>15.8</td>
</tr>
<tr>
<td>20Ni/SiO$_2$</td>
<td>0.68</td>
<td>10.7</td>
</tr>
<tr>
<td>30Ni/SiO$_2$</td>
<td>0.44</td>
<td>7.20</td>
</tr>
<tr>
<td>SBA-15</td>
<td>0.95</td>
<td>4.80</td>
</tr>
<tr>
<td>10Ni/SBA-15</td>
<td>0.56</td>
<td>6.80</td>
</tr>
<tr>
<td>20Ni/SBA-15</td>
<td>0.63</td>
<td>5.10</td>
</tr>
<tr>
<td>30Ni/SBA-15</td>
<td>0.50</td>
<td>4.60</td>
</tr>
</tbody>
</table>

In XRD analysis of the fresh catalysts, there is one wide diffraction peak in all catalysts, which was corresponding to amorphous SiO$_2$ and SBA-15 materials. No peak associated with the metallic (nickel, cobalt, and iron) phase are found in all catalysts, indicating the high dispersion of transition metal species or crystallites smaller than 3
nm may have formed in these catalysts.

### 4.3.5 XRD analysis of the used catalysts

Diffraction peaks of the catalysts were observed after steam reforming experiments were carried out over the catalysts as shown in Figure 4.7 (A) and (B). The crystallite size of the used catalysts are calculated by Sherre’s equation and the results are presented in Table 4.2.

![XRD pattern](image)

**Figure 4.7.** XRD pattern of the used catalysts; (A) SiO$_2$, (b) 10Co/SiO$_2$, (c) 10Fe/SiO$_2$, (d) 10Ni/SiO$_2$, (e) 20Ni/SiO$_2$, (f) 30Ni/SiO$_2$ and (B) (a) SBA-15, (b) 10Ni/SBA-15, (c) 20Ni/SBA-15, (d) 30Ni/SBA-15.

In the XRD analysis of used 10Co/SiO$_2$ and 10Fe/SiO$_2$ catalysts, the peak associate to metal oxides were detected and no metallic (Co and Fe) peaks were observed. However, in used 10Ni/SiO$_2$ catalyst, the peak corresponding to metallic Ni was observed. The crystallize size of CoO become significantly large in used catalysts and it was 34 nm while Fe$_2$O$_3$ and Ni crystallize sizes in used catalysts were 4.3 and 3.4 nm, respectively. Therefore, 10Co/SiO$_2$ catalysts showed lower performance than 10Fe/SiO$_2$ and 10Ni/SiO$_2$ catalysts. 10Ni/SiO$_2$ exhibited highest performance due to exist metallic Ni metal during the steam reaction reaction.

In the consideration of Ni metal loading effect in the used catalysts, the crystalline size of Ni metal maintained the same in the loading of 10% and 20% as shown in Figure 4.3 and Table 4.1. The crystallize size of these calystas are 3.4 - 4.6 nm. The peaks associate to Ni metal in used 30wt% Ni catalysts are larger and the crystallize size are
7.2 nm (30wt%Ni/SiO$_2$) and 8.5 nm (30wt%Ni/SBA-15), associate to aggregation of metal particles. From these result, it can be concluded that high metal loading > 20wt% can easily aggregate during the steam reforming process.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Co/SiO$_2$</td>
<td>34 (CoO)</td>
</tr>
<tr>
<td>10Fe/SiO$_2$</td>
<td>4.3 (Fe$_2$O$_3$)</td>
</tr>
<tr>
<td>10Ni/SiO$_2$</td>
<td>3.4 (Ni)</td>
</tr>
<tr>
<td>20Ni/SiO$_2$</td>
<td>4.3 (Ni)</td>
</tr>
<tr>
<td>30Ni/SiO$_2$</td>
<td>7.2 (Ni)</td>
</tr>
<tr>
<td>10Ni/SBA-15</td>
<td>4.6 (Ni)</td>
</tr>
<tr>
<td>20Ni/SBA-15</td>
<td>4.0 (Ni)</td>
</tr>
<tr>
<td>30Ni/SBA-15</td>
<td>8.5 (Ni)</td>
</tr>
</tbody>
</table>

Crystal size of Ni metal was calculated from the (111) reflection of Ni.

Crystal size of CoO was calculated from the (2 0 0) reflection of CoO.

Crystal size of Fe$_2$O$_3$ was calculated from the (3 1 0) reflection of Fe$_2$O$_3$.

Table 4.2. Crystallite size of the used catalysts

No significantly different in crystallite size of Ni particle was observed using different supports (SiO$_2$ and SBA-15) which indicates that supports not effected on the particle size of Ni catalysts.

4.3.6 Steam reforming reaction screening of Ni catalysts

In the catalytic steam reforming of biomass gasification, H$_2$ rich gas was produced by the thermal decomposition, and steam reforming of tar and active carbon. In this analysis, we considered the H$_2$ gas evaluation from the steam reforming of sawdust (cellulose). The steam reforming reaction analysis of the Ni/SiO$_2$ and Ni/SBA-15 catalysts are described in Table 4. The steam reforming reaction are as follows:

\[
\begin{align*}
\text{C}_6\text{H}_{10}\text{O}_5 + 7\text{H}_2\text{O} & \rightarrow 6\text{CO}_2 + 12\text{H}_2 \quad \text{reaction (1)} \\
\text{C}_6\text{H}_{10}\text{O}_5 + \text{H}_2\text{O} & \rightarrow 6\text{CO} + 6\text{H}_2 \quad \text{reaction (2)} \\
\text{CO} + 3\text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \text{reaction (3)}
\end{align*}
\]

If 100% of reaction (1) would occur, it means that the biomass is completely reformed with steam. The higher percentage of the reaction (1) was observed in the activity examinations with 20Ni/SiO$_2$, 10Ni/SBA-15 catalysts. The obtained products from these experiments showed higher H$_2$/CO ratio and that those catalysts were suitable in the H$_2$ fuel cell application. In the H$_2$ fuel cell application, H$_2$ rich product gas with very low composition of CO or zero % of CO gas is required because of the CO gas could damage to the fuel cell membrane system. The reaction (2) has advantage to use the product gas for the combustion and the other chemical production purpose. 10Ni/SiO$_2$ and 20Ni/SBA-15 catalysts showed higher percentage of reaction (2). The product gas from this experiments contained higher concentration of the combustible CO gas that it offered the high heating value gas. 20Ni/SBA-15 catalyst exhibited the higher CO and CH$_4$ concentrations in the product gases than 10Ni/SBA-15 catalysts. The possibility to occur reaction (3) was not desired because it consumed 3 mole of H$_2$ gas to 1 mole CH$_4$ formation. 20Ni/SBA-15 showed in low possibility to occur reaction (2) and highest H$_2$ formation and combustible gases (CO and CH$_4$) formation.

Table 4.3. Steam reforming reaction screening
Conclusion

The SiO$_2$ supported transition metal (cobalt, iron, and nickel) catalysts, and the SBA-15 supported (nickel and nickel-cobalt) catalysts were synthesized and evaluated the catalytic activity in the steam reforming of sawdust. In comparison between the performance of Ni, Co, and Fe catalysts, Ni catalyst showed the highest performance. Compared to SiO$_2$ supported catalysts, SBA-15 supported catalysts exhibited better catalytic activity. SBA-15 support also showed lower extent to occur methane formation reaction than the SiO$_2$. Among all of the catalysts in this work, 20wt% Ni/SBA-15 catalysts resulted in the best performance with higher Mc,GAS formation.

References


<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO /mmol</th>
<th>CO$_2$ /mmol</th>
<th>CH$_4$ /mmol</th>
<th>CO + CH$_4$ /mmol</th>
<th>H$_2$ /mmol</th>
<th>Percentage of reac.(1)$^a$</th>
<th>Percentage of reac. (2)$^b$</th>
<th>Percentage from reac(2)to(3)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Ni/SiO$_2$</td>
<td>1.68</td>
<td>4.98</td>
<td>0.3</td>
<td>1.98</td>
<td>13.40</td>
<td>72</td>
<td>28</td>
<td>15</td>
</tr>
<tr>
<td>20Ni/SiO$_2$</td>
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<td>7.55</td>
<td>0.46</td>
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<td>16.54</td>
<td>83</td>
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<tr>
<td>30Ni/SiO$_2$</td>
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<td>1.19</td>
<td>6.98</td>
<td>0.32</td>
<td>1.51</td>
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<td>20Ni/SBA-15</td>
<td>2.34</td>
<td>7.35</td>
<td>0.51</td>
<td>2.80</td>
<td>17.00</td>
<td>72</td>
<td>28</td>
<td>18</td>
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<td>30Ni/SBA-15</td>
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<td>16.79</td>
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</tr>
</tbody>
</table>

$^a$CO$_2$ / (CO+CH$_4$+CO$_2$) × 100

$^b$(CO+CH$_4$) / (CO+CH$_4$+CO$_2$) × 100

$^c$CH$_4$ / (CO+CH$_4$) × 100
CHAPTER 5
STEAM REFORMING OF TAR DERIVED FROM BIOMASS PYROLYSIS OVER SUPPORTED Ni-MnO\textsubscript{x}/SBA-15 CATALYST AT LOW TEMPERATURE

5.1 Introduction
Catalytic steam reforming of tar derived from biomass (CSRT-biomass) have been attracted much attention from both industrial and academic researchers due to its high conversion efficiency of biomass into fuels.\textsuperscript{1} This process usually operated in a temperature range of 873-1173 K due to the endothermic nature of the reforming reaction.\textsuperscript{2} Ni-based catalysts have been proven as one of the most effective transition metal catalyst. Unfortunately, they are easily deactivated by the carbon deposition and sintering of Ni\textsubscript{0} species.\textsuperscript{3-6} Therefore, the development in more stable Ni-based catalysts with high resistance to coke deposition and sintering are still required. Generally, a catalyst with small particle size and strong metal-support interaction can prevent sintering and carbon deposition.\textsuperscript{35} Catalyst synthesis procedure and choice of support material are crucial to obtain such kind of catalyst. Porous material with high internal surface area and large pore volume as support can provide spatial confinement to restrict the growth of metal nanoparticles and prevent the active particles from aggregation, and their channels can serve as the transfer paths for the reactant and products.\textsuperscript{16, 17} Mesoporous SBA-15 material have been proved to be a good support to dispersing and controlling metal particle size.\textsuperscript{18-20} It was reported that polyol such as ethylene glycol (EG) can deliver the metal species into the SBA-15 channel by simple impregnation method, producing highly dispersed metal nanoparticles.\textsuperscript{21, 22} To overcome carbon deposition on Ni catalysts, many Ni-based bimetallic catalysts such as Ni-CeO\textsubscript{2},\textsuperscript{8} Ni-Co,\textsuperscript{12, 33} Ni-Cu,\textsuperscript{7} Ni-Fe,\textsuperscript{9, 11, 12} and Ni-Mn\textsuperscript{10} have been developed. The improvement in catalytic performance of bimetallic was related to the formation of alloy particles and/or supply of oxygen from the second metal to the Ni metal. MnO\textsubscript{x} containing catalysts have been widely applied in many reactions, including NO\textsubscript{x} reduction,\textsuperscript{13, 14} and steam reforming,\textsuperscript{10, 15} owing to its excellent redox property. Koike et al.\textsuperscript{10} synthesized Ni/MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalysts by co-impregnation method and the performance of the catalysts were studied in the CSRT-biomass reaction. They reported that Ni/MnO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} catalysts showed higher performance than Ni/CeO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} catalysts. The supply of oxygen atoms from MnO\textsubscript{x} to Ni species enhanced the reaction between carbonaceous and oxygen on the Ni. Therefore, MnO\textsubscript{x} is a very interesting additive for the development of Ni-based steam reforming catalysts.

From the above consideration, the aim of this study was to synthesize highly dispersed Ni-MnO\textsubscript{x}/SBA-15 catalysts and evaluate the catalytic activity in the CSRT-biomass at low reaction temperature, 773 K. The catalysts were analyzed by X-ray diffraction (XRD), transmission electron microscope (TEM), temperature program reduction (TPR), N\textsubscript{2} adsorption-desorption and temperature program oxidation (TPO). The activities of the catalysts were discussed on the results of the steam reforming experiments and the characteristics of the catalysts.
5.2 Experimental

5.2.1 Preparation of SBA-15 with large pore size SBA-15

The larger pore size SBA-15 (pore size; 4.5 - 5 nm) was prepared by soft template procedure using surfactant (triblock copolymer Pluronic P123; PEO20PPO70PEO20) and Hexane (pore size expender as described in article 3.2.2. To access the influence of the synthesis conditions (aging temperature and aging time) on the pore structure of calcined SBA-15 material, three different kinds of SBA-15 materials; (A) Aging temp. 333 K and aging time 48 h, (B) Aging temp. 333 K and aging time 120 h, and (C) Aging temp. 353 K and aging time 48 h were prepared.

5.2.2 Catalyst preparation

Ni-MnOx/SBA-15 catalysts were synthesized by ethylene glycol assisted impregnation technique as described in article 3.3.2. The catalysts were calcined at 723 K and the calcined catalysts were 10Ni/SBA-15, 9Ni-1Mn/SBA-15, 7Ni-3Mn/SBA-15, 5Ni-5Mn/SBA-15 and 1Ni-9Mn/SBA-15.

5.2.3 Catalyst characterization

The specific surface area (BET method), pore volume and pore size distribution (according to the BJH method, desorption data was used for the determination of pore size distribution) of the catalysts was measured by N₂ adsorption-desorption at 77 K (Tristar3000). The XRD profiles (small-angle XRD and wide-angle XRD) of the catalysts were detected with Cu Kα radiation (Smart lab and Miniflux). TEM was used to confirm the particle size and size distribution of the metal species (JEM-2010HT). The reducibility of chemical species on the catalysts was examined by TPR with a mass spectrometer. Prior to TPR measurement, the catalysts were dried at 393 K for 1 h in Ar flow, and then temperature was raised from 323 K to 1173 K at a heating rate of 10 K/min under 10%H₂ in 30 ml/min Ar flow. The amount of deposited carbon/coke on the used catalysts was measured by TPO with 3%O₂ in 30 ml/min Ar flow. The procedure was the same with the TPR measurement.

5.2.4 Activity experiment

Catalytic activity tests were carried out in a two-stage fixed-bed reactor as described in the article 3.5.2. The catalyst was pre-reduced with an H₂/N₂ (30/30 ml/min) mixed gas at 773 K for 1 h.

5.3 Results and Discussion

5.3.1 N₂-physisorption of SBA-15 materials

Physical properties of the prepared SBA-15 materials were measured by N₂ adsorption. The adsorption-desorption isotherms are shown in Figure 5.1(A), (B) and (C) and the physical parameter are listed in Table 5.1. The isotherms for SBA-15 materials aged at 333 K featured sharp steps of capillary condensation in the relative
pressure interval from 0.65 to 0.9, indicating the presence of uniform large mesopores and their pore size were center at ~ 9 nm. The SBA-15 material with longer aging time, 120 h, showed a slightly wider relative pressure interval than that was aged for 48 h, mean wider pore size distribution. The isotherm for SBA-15 aged at 363 K had wide
relative pressure interval with two kinds of pore size distributions. It was due to evaporation of Hexane (used as micelle expender) during aging of precursor mixture at higher temperature (367 k) than boiling point (341 K) of Hexane.

Table 5.1 N\textsubscript{2}-physorption measurement results of the SBA-15 materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Material</th>
<th>S\textsubscript{BET} (m\textsuperscript{2}/g)</th>
<th>V\textsubscript{P} (cm\textsuperscript{3}/g)</th>
<th>V\textsubscript{MP} (cm\textsuperscript{3}/g)</th>
<th>D\textsubscript{BJH} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>SBA-15; 333 K &amp; 48 h</td>
<td>666</td>
<td>1.27</td>
<td>0.045</td>
<td>9.1</td>
</tr>
<tr>
<td>B</td>
<td>SBA-15; 333 K &amp; 120 h</td>
<td>670</td>
<td>1.41</td>
<td>0.053</td>
<td>9.0</td>
</tr>
<tr>
<td>C</td>
<td>SBA-15; 353 K &amp; 48 h</td>
<td>545</td>
<td>0.935</td>
<td>0.036</td>
<td>6.7/3.4</td>
</tr>
</tbody>
</table>

S\textsubscript{BET}: BET specific surface area, V\textsubscript{P}: total pore volume, V\textsubscript{MP}: micro-pore volume, D\textsubscript{BJH}: BJH pore diameter (taken as maximum point)

The specific surface area, total pore volume and pore size of sample C showed lower than that of samples A and B, indicates that aging temperature has significantly affected on surface properties in synthesis of SBA-15. No different in pore size was observed in sample A and B although total pore volume was slightly lower in sample A than sample B. For the preparation of the supported catalysts, sample A was chosen as a support due to require short aging time, providing desired pore size.

5.3.2 Activity of catalyst in CSTR-biomass

The yields of carbon products and the yield of product gases are shown in Figures 5.2 and 5.3, respectively. The production rate of product as a function of reaction time was described in Figure A4. In the case of MnO\textsubscript{x}/SBA-15 catalyst, a large amount of tar formed; while no residual tar was found in Ni/SBA-15 catalyst. This indicates the poor activity of MnO\textsubscript{x}/SBA-15 catalyst and it was not better than simple thermal decomposition of sawdust without a catalyst. In the Ni-MnO\textsubscript{x}/SBA-15 catalysts, tar conversion ability gradually increased with increasing Ni loading, probably due to the ability of C-C and C-H cleavage by Ni in the catalysts. In 9Ni-1Mn/SBA-15 catalyst, there was no tar remained and highest conversion for gas products was obtained. Very

![Figure 5.2](image-url)

Figure 5.2. The performance of the Ni-MnO\textsubscript{x}/SBA-15 catalysts in the steam reforming of sawdust; pyrolysis bed: 973 K and catalyst bed: 773 K.
small amount of coke (<1%) was observed in the Ni/SBA-15 with 0-5 wt% Mn addition to Ni catalysts. In MnOx/SBA-15 catalysts, the percentage of coke was slightly larger than the other catalysts, relating to its low steam reforming activity. The activity of the catalyst in the steam reforming of tar is reflected by the residual tar amount and the gas formation (H2, CO, CH4, and CO2). A change in selectivity of the product gas was observed by the introduction of Mn to Ni, and selectivity to H2 was improved. The 9Ni-1Mn/SBA-15 catalysts showed higher H2 yield than the other catalysts. In the catalytic steam reforming, common tar steam reforming reaction is

\[ C_nH_m + nH_2O \rightarrow nCO + (n+m/2)H_2 \] ................................................................. (1)

and followed by the secondary water gas shift reaction.

\[ CO + H_2O \leftrightarrow H_2 + CO_2 \] ................................................................. (2)

In Figure 5.2., it can be suggested that extent of WGS reaction was reduced by addition of Mn to Ni if it was considered from the resultant amount of CO and CO2. Therefore, the enhancement in H2 yield in bimetallic may be originated from the redox property, a result of the various oxidation state of MnOx like CeO2.

5.3.3 Characteristics of the fresh catalysts

The N2 adsorption-desorption isotherms together with pore size distribution of the catalysts can be seen in Figures 5.4. The physical properties of the catalysts are summarized in Table 5.1.

The isotherms of the Ni-MnOx/SBA-15 catalysts are type IV Langmuir isotherms with H 1 hysteresis loops, according to IUPAC classification. It represented the mesoporous nature of SBA-15.31 The surface area, pore volume and pore size of SBA-15 support were decreased by impregnation due to metal particles entered into the pores and took place in the porous structure.,20, 27 Therefore, the pore size of SBA-15 were changed and decreased by metal impregnation and resulted in pore size distribution with two center points. The surface area and pore volume of the
monometallic Ni/SBA-15 catalyst was larger than that of the Ni-MnOₓ/SBA-15 bimetallic catalysts. From these results, it can be expected that Mn addition to Ni/SBA-15 catalyst leads to migration of metal species further within the pores of mesoporous...

Figure 5.4. \( \mathrm{N}_2 \) adsorption-desorption isotherms and pore size distribution of the SBA-15 supported and Ni-MnOₓ/SBA-15 catalysts.
All catalysts possessed large surface area due to the nature of mesoporous SBA-15 supports, which afford for high metal dispersion.

The stability of mesoporous nature of SBA-15 supported Ni-MnO_x catalysts were further confirmed by small-angle XRD measurement and the profiles are described in Figure 5.5. In Figure 5.5, it can be seen that SBA-15 material show a sharp XRD peak at d_{100} (d: interplanar distance) and two minor peaks corresponding to d_{110} and d_{200} reflections, indicating highly order two-dimensional hexagonal material. The Ni-MnO_x/SBA-15 catalysts displayed a significantly decline in peak intensity, corresponding to a reduction of degree of porous organization.

Wide-angle XRD measurement was also conducted to access the diffraction phases of metal species and XRD profiles are presented in Figure 5.6. In 10Ni/SBA-15 catalyst, three weak and diffuse diffraction peaks, assigned to NiO, were detected. It suggests
that some larger NiO particles are dispersed on the outside of the mesoporous channel of SBA-15 support. In the Ni-MnO\textsubscript{x}/SBA15 and MnO\textsubscript{x}/SBA-15 catalysts, no diffraction peaks were detected. It means all the catalysts have small particle size and high dispersion in the SBA-15 supports.\(^{18}\)

![TEM images](image)

**Figure 5.7.** TEM image of the Ni-MnO\textsubscript{x}/SBA-15 catalysts; (a) 10Ni, (b) 9Ni-1Mn, (c) 7Ni-3Mn, (d) 5Ni-5Mn, (e) 1Ni-9Mn, (f) 10Mn.

TEM images and particle size distribution of the catalysts are presented in Figure 5.7 and 5.8. TEM observation confirmed that the nanoparticles (NPs) were distributed homogeneously with high dispersion in the mesoporous channel of the SBA-15, which was in good agreement with XRD results. The average metal particle size of 10Ni/SBA-15 catalyst was 4.53 nm and it was slightly larger than the bimetallic Ni-MnO\textsubscript{x}/SBA-15 catalysts. In the bimetallic Ni-MnO\textsubscript{x}/SBA-15 catalysts, the remarkable difference in the sizes of the nanoparticles (NPs) was not observed and they are smaller than 3 nm.

| Table 5.2. Physical properties of the Ni-MnO\textsubscript{x}/SBA-15 catalysts From (BET, XRD and |
TPR profiles of the catalysts are shown in Figure 5.9 together with the amount of H$_2$ consumption. H$_2$ consumptions were calculated from TPR profiles up to 773 K because the catalysts were pre-reduced at 773 K in these experiments. The hydrogen reduction of the Ni/SBA-15 showed a low-temperature peak (453 K) and a very broad

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$S_{BET}$</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>$D_{BJH}$ (nm)</th>
<th>$d_{100}$ (nm)</th>
<th>$D_{M}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>666</td>
<td>1.27</td>
<td>9.10</td>
<td>12.98</td>
<td>-</td>
</tr>
<tr>
<td>10Ni/SBA-15</td>
<td>629</td>
<td>0.817</td>
<td>3.6/5.3</td>
<td>12.98</td>
<td>4.53</td>
</tr>
<tr>
<td>9Ni-1Mn/SBA-15</td>
<td>590</td>
<td>0.77</td>
<td>3.6/5.3</td>
<td>12.98</td>
<td>2.47</td>
</tr>
<tr>
<td>7Ni-3Mn/SBA-15</td>
<td>569</td>
<td>0.72</td>
<td>4.0/6.2</td>
<td>12.98</td>
<td>2.34</td>
</tr>
<tr>
<td>5Ni-5Mn/SBA-15</td>
<td>558</td>
<td>0.71</td>
<td>4.0/6.2</td>
<td>13.38</td>
<td>2.99</td>
</tr>
<tr>
<td>1Ni-9Mn/SBA-15</td>
<td>556</td>
<td>0.74</td>
<td>3.6/5.3</td>
<td>13.38</td>
<td>2.25</td>
</tr>
<tr>
<td>10Mn/SBA-15</td>
<td>516</td>
<td>0.76</td>
<td>3.6/5.3</td>
<td>12.98</td>
<td>2.88</td>
</tr>
</tbody>
</table>

$S_{BET}$: BET specific surface area, $V_p$: total pore volume, $D_{BJH}$: BJH pore diameter (taking at their maximum points), $d_{100}$: interplaner distance (XRD), $D_M$: diameter of metal particles (calculated from avg. of 100 particles from TEM image)

**Figure 5.8.** Size distribution of metal particles of the Ni-MnO$_x$/SBA-15 catalysts obtained from the TEM image.
peak with a wide temperature range (493-973 K). The low-temperature reduction peak may be assigned to the reduction of NiO on the surface of SBA-15 to metallic Ni or the reduction of surface oxygen species.\textsuperscript{28} The broad peak represented reduction behavior of highly dispersed NiO NPs in the channel of the SBA-15 framework to Ni\textsuperscript{0}.\textsuperscript{19,21} In the MnO\textsubscript{x}/SBA-15 catalyst, two overlap features are detected in the temperature range of 423-643 K which can be possibly attributed to successive reduction of Mn\textsuperscript{4+}→Mn\textsuperscript{3+}→Mn\textsuperscript{2+}.\textsuperscript{20} In the Ni-MnO\textsubscript{x}/SBA-15 catalysts, the low-temperature peaks grew up with increasing Mn loading to Ni and these peaks slightly shift to lower temperature compared with MnO\textsubscript{x}/SBA-15 catalyst. It can be possibly due to interaction of NiO and MnO\textsubscript{x} on the surface of SBA-15 or MnO\textsubscript{x} reduction and/or increased in surface oxygen species.\textsuperscript{28,29} The high temperature peak of NiO also shifted to lower temperature by increasing Mn addition to Ni, implying that enhanced dispersion of Ni NPs.\textsuperscript{30} The amount of H\textsubscript{2} consumptions are lower than the total required H\textsubscript{2} for complete reduction in all catalysts. This indicated the metal NPs are highly dispersed into the porous channels of the SBA-15 support. Wang et al.\textsuperscript{34} reported that the reduced Ni particles are dispersed evenly on the surface of pores.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{TPR profiles of the Ni-MnO\textsubscript{x}/SBA-15 catalysts.}
\end{figure}

5.3.4 Characteristics of the used catalysts

The structure of the used catalysts were analyzed by XRD (small-angle and wide-angle) and the results are displayed in Figure 5.10 and 5.11.

There were no changes in the structure of used catalysts according to the results of the small-angle and wide-angle XRD measurements, indicating the catalysts are stable in the oxidation and reduction condition during CSRT-biomass experiments.
Discussion on promotion effect of Ni-MnO\textsubscript{x}/SBA-15 catalysts

The activities of the 10Ni/SBA-15 and 9Ni-1Mn/SBA-15 catalysts showed comparable or higher performance than that of the reference catalysts\textsuperscript{5, 8-10, 12, 33} especially in coke % and H\textsubscript{2}/CO. The high activities were attributed to small metal particle size and high dispersion of metal NPs in the SBA-15 supports. Addition of (1 wt\%) of Mn to 10Ni/SBA-15 catalyst further enhanced the performance of catalyst. It was due to increased dispersion of Ni particles and the synergy effect between Ni metal and MnO\textsubscript{x}, supply of O\textsubscript{2} from MnO\textsubscript{x} to active Ni species, which promoted the reaction between carbonaceous species and oxygen species on the Ni surface. High in H\textsubscript{2} yield originated from the two-stage pyrolysis-catalytic steam reforming system which was proved to be suitable for hydrogen rich gas production.

Figure 5.10. Small-angle XRD profiles of the used Ni-MnO\textsubscript{x}/SBA-15 catalysts; detected by using Cu K\textalpha radiation.

Figure 5.11. Wide-angle XRD profiles of the used Ni-MnO\textsubscript{x}/SBA-15 catalysts; detected by using Cu K\textalpha radiation.
5.4 Conclusion

In the CSRT-biomass experiments, the activities of the Ni-MnOx/SBA-15 catalysts showed as high as that of the Ni/SBA-15 catalyst while MnOx/SBA-15 catalyst exhibited low activity. Addition of small amount (1 wt%) of Mn to Ni (9Ni-1Mn/SBA-15) catalyst exhibited higher performance in terms of product gas formation % and H2 yield than the corresponding monometallic 10Ni/SBA-15 catalysts. Very low carbon deposition amounts (< 1 wt%) and complete tar conversion were observed in 10Ni/SBA-15 and 9/7/5Ni-1/3/5Mn/SBA-15 catalysts. For 10Ni/SBA-15 catalyst, gas formation % and H2 formation amounts were 70% and 45 mmol/g biomass. For 9Ni-1Mn/SBA-15 catalyst, gas formation % was 72 % and H2 formation amount was 55 mmol/g biomass.

References
CHAPTER 6
STEAM REFORMING OF BIOMASS DERIVED-TAR OVER Ni-MnOx/SBA-15 CATALYSTS: ROLE OF METAL-SUPPORT INTERACTION AND CATALYTIC ACTIVITY

6.1 Introduction

Hydrogen’s share in the energy market is increasing with the implementation of fuel cell systems and the growing demand for zero-emission fuels. Approximately 95% of hydrogen produced today is from fossil fuel sources. Since biomass is a renewable and consumes atmospheric CO₂ during growth, it can have a small net CO₂ impact compared to fossil fuels. Biomass has the potential to accelerate the realization of hydrogen as a major fuel of the future. Gasification of biomass represents an efficient way to generate energy with high efficiency and low environmental impacts. In the pyrolysis of biomass, 50-70 wt% of product fraction is the organic fraction/tars that may cause problems in downstream equipment. Tar removal can be accomplished by several routes, including physical separation, thermal cracking and catalytic tar conversion. Catalytic steam reforming process appears promising, because it can convert tar into synthesis gas at the same or even lower temperature than the gasification, which will improves the carbon efficiency and entire process efficiency.

Ni-based catalyst received the most attention for industrial applicable steam reforming catalyst. However, easily catalyst deactivation through metal sintering and coke deposition is considered the major challenge to be addressed. Many efforts have been conducting by modifying the chemical composition of catalyst support or/and by promoting the catalyst with additives for the development of more stable Ni-based catalyst with high resistance to carbon deposition and sintering. The influential factors on the catalyst activity and stability are found to be the metal particle size and dispersion, strong metal-support interaction and the catalyst reducibility.

It was recently reported that the development of tar steam reforming catalysts such as Ni/Mg/Al, Ni-Fe/Mg/Al and Ni-Cu/Mg/Al by using hydrotalcite-like compounds, provides active and stable catalysts. D. Li et. al. reported that formation of nanocomposite in the Ni/Mg/Al catalyst enhanced the interaction between the Ni metal particle and oxide support, suppressed the aggregation of metal particles and exhibited higher activity, resistance to coke deposition, and stability than Al₂O₃- and MgO-supported Ni catalysts. D. Li et. al. reported that the formation of uniform Ni-Fe alloy and Ni-Cu alloy nanoparticles in the Ni-Fe/Mg/Al and Ni-Cu/Mg/Al catalysts exhibited very high activity for the steam reforming of biomass tar.

Apart from the metal oxide supported steam reforming catalysts, the supports with high surface area and large pore volume have been attracting increasing attention. Among them, mesoporous SBA-15 material is interesting, and have been proved to be a good support to dispersing and controlling metal particle size. In addition, the strategy of stabilizing the metal nanoparticles by encapsulating into the porous channel of SBA-15 material have been explored. Therefore, the used of the SBA-15 supported Ni-based metal catalysts have been applied in many reactions, including ethanol steam
reforming,\textsuperscript{15,19} steam reforming in cellulose decomposition,\textsuperscript{14,18,20} steam reforming of biomass tar model compound,\textsuperscript{21} although there are very few or no report on the catalytic steam reforming biomass derived tar (CSRT-biomass) using the SBA-15 supported Ni-based catalyst. It have been known that strong metal-support interaction (SMSI) is one of the important factors on catalytic activity and stability.\textsuperscript{5,11} Compare with the metal oxide and Al\textsubscript{2}O\textsubscript{3} supports, SiO\textsubscript{2} support has a low interaction with the active metal sites.\textsuperscript{5,9} In the catalyst preparation, calcination temperature is one of the important parameter to enhance the metal-support interaction, and the interaction between two metal species in the supported bimetallic catalysts. Therefore, the optimization of the calcination temperature is always required, due to their impact on the metal particle size and dispersion, metal-support interaction, and consequently the catalytic performance.\textsuperscript{11}

Recently, we synthesized Ni-MnO\textsubscript{x}/SBA-15 catalysts by ethylene glycol assisted impregnation technique and they are calcined at 723 K.\textsuperscript{22} The activities of catalysts are examined in biomass derived tar steam reforming reaction and the catalysts showed very high activities in this process. It was due to very small particle size (< 5nm) and high dispersion of metal particles into the porous channel of SBA-15 support. Addition of the small amount of Mn to Ni (9Ni-1Mn/SBA-15) catalysts further improve the activity and H\textsubscript{2} yield than that of the corresponding monometallic 10Ni/SBA-15 catalysts due to increase dispersion of Ni particles and the synergy effect between Ni metal and MnO\textsubscript{x}. In this article, the Ni-MnOx/SBA-15 catalysts are prepared at the calcination temperature of 973 K and the catalytic activities was conducted in CSTR-biomass. The effects of calcination temperature and reduction temperature of the catalysts in the CSRT-biomass are examined and discussed based on the results of the activity experiments and characteristics of the catalysts.

6.2 Experimental
6.2.1 Preparation of SBA-15 with large pore size
The larger pore size SBA-15 (pore size; 4.5 - 5 nm) was prepared by soft template procedure using surfactant (triblock copolymer Pluronic P123; PEO20PPO70PEO20) and Hexane (pore size expander as described in article 3.2.2).

6.2.2 Catalyst preparation
Ni-MnO\textsubscript{x}/SBA-15 catalysts were synthesized by ethylene glycol assisted impregnation technique as described in article 3.3.2. The catalysts were calcined at 723 K and 973 K, and the prepared calcined catalysts were 10Ni/SBA-15-C723, 9Ni-1Mn/SBA-15-C723, 7Ni-3Mn/SBA-15-C723, 10Ni/SBA-15-C973, 9Ni-1Mn/SBA-15-C973 and 7Ni-3Mn/SBA-15-C972.

6.2.3 Catalyst characterization
The specific surface area of the catalysts was measured by N\textsubscript{2} adsorption-desorption at 77 K (Tristar3000). The XRD profiles of the catalysts were detected with Cu K\textsubscript{a} radiation. TEM was used to confirm the particle size and size distribution of the metal species (JEM-2010HT). The reducibility of chemical species on the catalysts was examined by TPR with a mass spectrometer. Prior to TPR measurement, the catalysts
were dried at 393 K for 1 h in Ar flow, and then temperature was raised from 323 K to 1173 K at a heating rate of 10 K/min under 10%H₂ in 30 ml/min Ar flow. The amount of deposited carbon/coke on the used catalysts was measured by TPO with 3%O₂ in 30 ml/min Ar flow. The procedure was the same with the TPR measurement. Crystallite size of used catalysts were measured by XRD.

6.2.4 Activity experiment
Catalytic activity tests were carried out in a two-stage fixed-bed reactor as described in the article 3.5.2. The calcined catalysts were pre-reduced with an H₂/N₂ (30/30 ml/min) mixed gas at 773 K or 973 K for 1 h in order to study effect of reduction temperature of catalysts in the CSRT-biomass reaction.

6.3 Results and discussion
6.3.1 Activity of catalyst in CSTR-biomass
Activities of the catalysts, Ni-MnOₓ/SBA-15-C723 and Ni-MnOₓ/SBA-15-C973, were investigated in the CSRT-Biomass reaction. Ni-MnOₓ/SBA-15-C723 catalysts were pre-reduced at 773 K for 1 hr and Ni-MnOₓ/SBA-15-C973 catalysts were pre-reduced at two different reduction temperatures, 773 K and 973 K, before activity experiments. The effect of catalyst calcination temperature was examined on Ni-MnOₓ/SBA-15-C723 and Ni-MnOₓ/SBA-15-C973. The effect of catalyst reduction temperature was investigated on Ni-MnOₓ/SBA-15-C973 catalysts. Since conversion to product gas and amount of H₂ formation are the main important parameters to be taken into account in the CSRT-biomass process, the performance of catalysts were considered from these aspects.

6.3.1.1 Effect of calcination temperature
The yields of carbon product and gaseous product are shown in Figure 6.1. The production rate of product gas as a function of reaction time was shown in Figure A5. It can be seen in Figure 6.1(A) that complete tar conversion into gaseous product was achieved in the 10Ni/SBA-15 and 9Ni-1Mn/SBA-15 catalysts. However, residual tar were observed in 7Ni-3Mn/SBA-15 catalysts due to decrease in available of active Ni metal species. The amounts of deposited carbon, coke, were very low (< 0.8%) in all catalysts and almost the same amount upon the change in calcination temperature of catalysts. The higher temperature calcined catalysts, 10Ni/SBA-15-C973 and 9Ni-1Mn/SBA-15-C973, further enhanced in product formation % than low temperature calcined catalysts, 10Ni/SBA-15-C723 and 9Ni-1Mn/SBA-15-C723. This was due to the effect of strong metal support interaction (SMSI) which was approved by XRD and TPR measurement results. In contract, the gas formation % of higher temperature calcined catalyst, 7Ni-3Mn/SBA-15-C973, was lower than that of 7Ni-3Mn/SBA-15-C723 catalyst. It can be negative effect of very SMSI, leading to encapsulation of metal particle by support material and lost the active sites.³⁷
Since heterogeneous catalytic reactions including tar cracking, steam reforming, CO\textsubscript{2} reforming and water-gas shift reaction, the Ni-MnO\textsubscript{x}/SBA-15-C723 and Ni-MnO\textsubscript{x}/SBA-15-C973 catalysts play different roles in the selectivity of product gas. The formation amount of gas are shown in Figure 6.1(B) and volume % of product gas and are listed in Table 6.1. H\textsubscript{2} yield are higher in in the higher temperature calcined catalysts, 10Ni/SBA-15-C973 and 9Ni-1Mn/SBA-15-C723, than corresponding lower temperature calcined catalysts, indicating significant role of SMSI in H\textsubscript{2} production. The enhancement of H\textsubscript{2} production was more significant in 10Ni/SBA-15-C973 catalyst and it exhibited the highest H\textsubscript{2} yield among in all of the other catalyst in this experiment. This result strongly associated with Ni\textsubscript{2}SiO\textsubscript{4} phase which was appeared by SMSI between Ni metal and SBA-15 support. In 7Ni-3Mn/SBA-15-C973 catalyst, H\textsubscript{2} production amount was slightly lower than 7Ni-3Mn/SBA-15-C723 although the volume % of H\textsubscript{2} in product gas was high. If consider from H\textsubscript{2} yield, the catalyst can be order as 10Ni/SBA-15-C9673 > 9Ni-1Mn/SBA-15-C973 > 9Ni-1Mn/SBA-15-C723 > 7Ni-3Mn/SBA-15-C973 > 7Ni-3Mn/SBA-15-C973 > 7Ni-3Mn/SBA-15-C973 > 7Ni-3Mn/SBA-15-C973 > 7Ni-3Mn/SBA-15-C973 > 10Ni/SBA-15-C723 > 10Ni/SBA-15-C723. If consider from product gas yield %, the order be 9Ni-1Mn/SBA-15-C973 > 9Ni-1Mn/SBA-15-

6.3.1.2 Effect of reduction temperature

The effect of catalyst reduction temperature in CSRT-biomass reaction was investigated on 10Ni/SBA-15-C973 and 9Ni-1Mn/SBA-15-C973 catalysts. Catalysts are reduced at two different temperature 773 K and 973, K prior to carry out activity experiments. Figure 3 represents carbon based yield and yield of product gas. The production rate of product gas as a function of reaction time was shown in Figure A6.

In Figure 3, it can be seen that the product gas % and H₂ yields were decreased by higher reduction temperature in both 10Ni/SBA-15 and 9Ni-1 Mn/SBA-15 catalysts. This indicates that higher catalyst reduction temperature have negative impact in the performance of catalysts. This phenomena can be explained that higher temperature, 973 K, resulted in metal agglomeration and reduced active metal sites while lower reduction temperature, 773 K, supported to obtain small active metal particle and high dispersion into the SBA-15 support during the reduction step of catalysts. Product gas yields were decreased from 72% to 70% in 10Ni/SBA-15-973 catalysts and 73% to 64% in 9Ni-1Mn/SBA-15-C973 catalysts. H₂ formation amounts (mmol/g biomass) also were decreased from 60 to 54 in 10Ni/SBA-15-C973 catalysts and 58 to 52 in 9Ni-1Mn/SBA-15-C973 catalysts.

Table 6.1. Volume percentage of the product gas from steam reforming experiments

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reduction temperature (K)</th>
<th>Volume percentage of product gas*</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Ni-C723</td>
<td>773</td>
<td>CO 5.9</td>
</tr>
<tr>
<td>9Ni-1Mn-C723</td>
<td>773</td>
<td>CO 9.0</td>
</tr>
<tr>
<td>7Ni-3Mn-C723</td>
<td>773</td>
<td>CO 12.0</td>
</tr>
<tr>
<td>10Ni-C973</td>
<td>773</td>
<td>CO 9.8</td>
</tr>
<tr>
<td>9Ni-1Mn-C973</td>
<td>773</td>
<td>CO 14.0</td>
</tr>
<tr>
<td>7Ni-3Mn-C973</td>
<td>773</td>
<td>CO 14.3</td>
</tr>
<tr>
<td>10Ni-C973</td>
<td>973</td>
<td>CO 16.4</td>
</tr>
<tr>
<td>9Ni-1Mn-C973</td>
<td>973</td>
<td>CO 16.2</td>
</tr>
</tbody>
</table>

*mole of CO or CH₄ or CO₂ or H₂/ total mole of (CO+CH₄+CO₂+H₂)
6.3.2 Characteristics of the fresh catalysts

The N$_2$ adsorption-desorption isotherms and pore size distribution of the Ni-MnO$_x$/SBA-15-C723 and Ni-MnO$_x$/SBA-15-C973 catalysts are shown in Figure 6.3 and 6.4, respectively. The physical properties (BET analysis) and average metal particles sizes (TEM observation and XRD measurement) of the catalysts are summarized in Table 6.2.

The isotherms of the Ni-MnO$_x$/SBA-15 catalysts are type IV Langmuir isotherms with H 1 hysteresis loops, according to IUPAC classification. It represented the mesoporous nature of SBA-15. 27 BET surface area, pore volume and pore size of SBA-15 support (Table 6.2) were decreased by metal impregnation due to metal particles entered into the pores and took place in the porous channel of SBA-15 support. 16, 28 The pore diameters in 9Ni-1Mn/SBA-15-C973 and 7Ni-3Mn/SBA-15-C973 were larger than that of the other catalysts and just slightly smaller than SBA-15 support, expecting
that MSI in these two catalysts were much stronger and the metal particles were flattened by its effect.\textsuperscript{40} Losses in surface area of the Ni-MnO\textsubscript{x}/SBA-15-C973 catalysts were larger than that of the Ni-MnO\textsubscript{x}/SBA-15-C723, associating with high temperature thermal treatment that broken some parts of mesoporous wall.

The stability of porous structure by metal impregnation was further confirmed by small-angle XRD measurement and the XRD profiles are displayed in Figure 6.5 and 6.6.

Figure 6.3. \textsuperscript{40}N\textsubscript{2} adsorption-desorption isotherms and pore size distribution of Ni-MnO\textsubscript{x}/SBA-15-C723 catalysts.

The intensity of diffraction peaks (100, 110 and 200 planes) was reduced, correspond to decrease of order of porous structure by metal impregnation. Interplaner distance, d\textsubscript{100}, planes of Ni-MnO\textsubscript{x}/SBA-15-C723 catalysts were 12.98 nm and the sthe same with that of SBA-15 support. In higher temperature calcined Ni-MnO\textsubscript{x}/SBA-15-C973
catalysts, d₁₀₀ plane were slightly reduced and these were 12.6 nm.

Wide-angle XRD patterns of the Ni-MnOₓ/SBA-15-C723 and Ni-MnOₓ/SBA-15-C973 catalysts are shown in Figure 6.7. In the Ni-MnOₓ/SBA15-C723 catalysts [Figure 6.7(A)], no diffraction peaks were detected for 10Ni/SBA-15-C723 catalyst in which three weak and diffuse diffraction peaks, assigned to NiO, were detected. It means all the catalysts have small particle size and high dispersion in the SBA-15 supports.¹⁴

![Figure 6.4. N₂ adsorption-desorption isotherms and pore size distribution of the Ni-MnOₓ/SBA-15-C973 K.](image)

In the case of 10Ni/SBA-15-C973 [Figure 6.7(A)], the diffraction peaks of NiO at 2θ = 37.3, 43.3 and 62.9 (JCPDS 047-1049) were slightly shifted to the lower angles, 0.1-0.11 degree, which can be due to the interaction of NiO and SiO₂, and therefore, Ni₂SiO₄ phases were detected. The diffraction peaks of NiO in the 9Ni-1Mn/SBA-15-
C973 and 7Ni-3Mn/SBA-15-C973 become weaker and wider that the peak shifts were also observed. The weaker and wider peaks are indicative of the effect of Mn addition to Ni that formed smaller particle size.\textsuperscript{34} The peak shift is interpreted by the formation of Ni-Mn alloy,\textsuperscript{13, 35, 36} and NiO, NiMn$_2$O$_4$ and Ni$_2$SiO$_4$ phases are overlap in these peaks. In Mn/SBA-15-C973 catalyst, weak and diffused peaks of different kind of MnO$_x$ were detected.

**Figure 6.5.** Small-angle XRD patterns of Ni-MnO$_x$/SBA-15-C723 catalysts; detected by Cu K\(\alpha\) radiation.

**Figure 6.6.** Small-angle XRD patterns of Ni-MnO$_x$/SBA-15-C973 catalysts; detected by Cu K\(\alpha\) radiation.
The metal particle sizes in the fresh Ni-MnO\textsubscript{x}/SBA-15-C723 catalysts were calculated from TEM measurements and TEM images of the Ni-MnO\textsubscript{x}/SBA-15-723 catalysts can be seen in Figure 5.4. The particle sizes of the Ni-MnO\textsubscript{x}/SBA-15-973 catalysts were calculated from wide-angle XRD measurement in which it was assumed assuming the metal particles are NiO and calculated from (200) reflection of NiO.

**Table 6.2.** The summary of BET, XRD and TEM characterization the SBA-15 supported catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>S\textsubscript{BET} (m\textsuperscript{2}/g)</th>
<th>V\textsubscript{total pore} (cm\textsuperscript{3}/g)</th>
<th>D\textsubscript{BJH} (nm)</th>
<th>D\textsubscript{100} (nm)</th>
<th>D\textsubscript{M1} (nm)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>666</td>
<td>1.27</td>
<td>6.48</td>
<td>12.98</td>
<td>-</td>
</tr>
<tr>
<td>10Ni; C723</td>
<td>629</td>
<td>0.817</td>
<td>4.08</td>
<td>12.98</td>
<td>4.53*</td>
</tr>
<tr>
<td>9Ni-1Mn; C723</td>
<td>590</td>
<td>0.77</td>
<td>5.23</td>
<td>12.98</td>
<td>2.47*</td>
</tr>
<tr>
<td>7Ni-3Mn; C723</td>
<td>569</td>
<td>0.724</td>
<td>4.17</td>
<td>12.98</td>
<td>2.34*</td>
</tr>
<tr>
<td>10Ni; C973</td>
<td>503</td>
<td>0.79</td>
<td>5.03</td>
<td>12.6</td>
<td>8.93*</td>
</tr>
<tr>
<td>9Ni-1Mn; C973</td>
<td>499</td>
<td>0.91</td>
<td>5.61</td>
<td>12.6</td>
<td>5.26*</td>
</tr>
<tr>
<td>7Ni-3Mn; C973</td>
<td>398</td>
<td>0.74</td>
<td>5.74</td>
<td>12.6</td>
<td>3.72*</td>
</tr>
</tbody>
</table>

*TEM

*assuming the metal particles are NiO and calculated from (200) reflection of NiO.

The metal particle sizes in the fresh Ni-MnO\textsubscript{x}/SBA-15-C723 catalysts were calculated from TEM measurements and TEM images of the Ni-MnO\textsubscript{x}/SBA-15-723 catalysts can be seen in Figure 5.4. The particle sizes of the Ni-MnO\textsubscript{x}/SBA-15-973 catalysts were calculated from wide-angle XRD measurement in which it was assumed...
that they are NiO and/or Ni. Scherrer equation was used to calculate the size of metal particles from the (111) reflection of Ni and (200) reflection of NiO and reported in Table 6.2.

TPR profiles of the Ni-MnO<sub>x</sub>/SBA-15 catalysts calcined at 723 K and 973 K are shown in Figure 6.8. TPR measurement can represent to determine the reducibility, dispersion and location of metal species, and the metal-support interaction.\textsuperscript{21}

Figure 6.8. TPR profiles of the (A) Ni-MnO<sub>x</sub>/SBA-15-C723 catalysts and (B) Ni-MnO<sub>x</sub>/SBA-15-C973 catalysts.

In Figure 6.8 (A), it can be seen that the hydrogen reduction of the Ni/SBA-15-C723 showed a low-temperature peak centered at 453 K and a very broad high temperature peak centered at 768 K. The low-temperature peak may be assigned to the reduction of NiO on the surface of SBA-15 to metallic Ni or reduction of surface oxygen species.\textsuperscript{29} Since the reduction of unsupported NiO is known to occur around 673 K,\textsuperscript{26} the high temperature broad peak represented reduction behavior of highly dispersed NiO nanoparticles (NPs) in the channel of the SBA-15 framework to Ni\textsuperscript{0}.\textsuperscript{15,28} In contrast, the reduction peaks of the 10Ni/SBA-15-C973 catalyst [Figure 6.8.(B)] significantly shifted to more higher reduction temperature with two stage reduction
behavior. The first peak at 808 K corresponds to reduction of highly dispersed NiO NPs in the channel of the SBA-15 framework to Ni. The second reduction peak at 1031 K attributes to the formation of NiO-Si species owing to strong metal-support interaction. In TPR profile of MnO/SBA-15-C723 catalyst [Figure 6.8.(A)], two overlap features were detected and the main peak was centered at 532 K, possibly attributed to successive reduction of MnO in the porous channel of SBA-15 to MnO, as MnO is irreducible throughout the temperature range. In the MnO/SBA-15-C973 catalyst, the reductions occur at much higher temperature with a maximum peak at 673 K, which was concerned with the SMSI to form MnSiO3. Therefore, it was indicated that higher calcination temperature, 973K, lead to occur metal-silicate phase and enhanced metal-support interaction.

In the TPR measurement of Ni-MnO/SBA-15-C723 bimetallic catalysts, low-temperature peaks grew up with increasing Mn loading to Ni and these peaks slightly shift to lower temperature compared with MnO/SBA-15 catalyst. It can be possibly due to interaction of NiO and MnO on the surface of SBA-15 or MnO reduction and/or increased in surface oxygen species. High temperature peak of NiO also shifted to lower temperature by increasing Mn addition to Ni, implying that enhanced dispersion of Ni NPs.

In the TPR profiles of higher temperature calcined bimetallic, two reduction peaks are detected in 9Ni-1Mn/SBA-15-C973 catalyst. The first peak shifted to lower temperature as compared to 10Ni/SBA-15-C973, indicates the emergence of different oxide species that was probably reduction of NiMn2O4 (confirmed by XRD result). The second peak corresponds to reduction of Ni2SiO4 to metallic Ni. The shift to lower reduction temperature was more significant in 7Ni-3Mn/SBA-15-C973 catalyst in which almost one broad peak was observed and it includes reduction of NiO, NiMn2O4 and Ni2SiO4 species.

The amount of H2 consumption was calculated from the TPR profiles and they are described in Table 6.3.

<table>
<thead>
<tr>
<th>catalysts</th>
<th>H2 requireda (mmol/g catal.)</th>
<th>H2 uptakeb (mmol/g catal)</th>
<th>H2 uptakec (mmol/g catal)</th>
<th>Ni-based reduction degree d ( %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Ni-C723</td>
<td>1.704</td>
<td>0.695</td>
<td>-</td>
<td>41</td>
</tr>
<tr>
<td>9Ni-1Mn-C723</td>
<td>1.534</td>
<td>0.182</td>
<td>0.652</td>
<td>38</td>
</tr>
<tr>
<td>7Ni-3Mn-C723</td>
<td>1.193</td>
<td>0.546</td>
<td>0.53</td>
<td>31</td>
</tr>
<tr>
<td>10Ni-C972</td>
<td>1.704</td>
<td>-</td>
<td>1.02</td>
<td>60/90</td>
</tr>
<tr>
<td>9Ni-1Mn-C973</td>
<td>1.534</td>
<td>0.182</td>
<td>0.709</td>
<td>42/93</td>
</tr>
<tr>
<td>7Ni-3Mn-C973</td>
<td>1.193</td>
<td>0.546</td>
<td>0.845</td>
<td>50/92</td>
</tr>
</tbody>
</table>

a Total H2 required to complete reduction of 10wt% Ni-Mn/SBA-15 catalysts
b H2 consumption up to 773 K in TPR profile
c H2 consumption up to 973 K in TPR profile
dcalculated on the basic of TPR; assuming that NiO +H2→Ni + H2O

H2 uptakes for the Ni-MnO/SBA-15-C723 catalysts were calculated from TRR profiles up to 773 K because they were pre-reduced at 773 K. In the Ni-MnO/SBA-15-C973 catalysts, pre-reduction was done at 773 K and 973 K that H2 uptakes were
calculated up to 773 K and 973 K from the TPR profiles. In Table 2, it can be seen that H₂ consumption are lower than the total required H₂ for complete reduction in all catalysts. This indicated the metal NPs are highly dispersed into the porous channels of the SBA-15 support. Wang et al. ⁴⁴ reported that the reduced Ni particles are dispersed evenly on the surface of pores.

6.3.3 XRD results of the used catalysts

The crystallite sizes of the catalysts and the stability of the structure of catalysts after catalytic steam reforming experiments were determined by XRD measurements. XRD patterns are shown in Figure 6.9 and 6.10. The metal particle sizes calculated from wide-angle XRD results and the plane distance of calculated from small-angle XRD results are listed in Table 6.3.

**Figure 6.9.** Wide-angle XRD pattern of the used Ni-MnOₓ/SBA-15 catalysts; (A) calcined at 723 K and reduced at 773 K, (B) calcined at 973 K and reduced at 773 K and (C) calcined at 973 K and reduced at 973 K.
Figure 6.10. Small-angle XRD pattern of the used Ni-MnO/SBA-15 catalysts; (A) calcined at 723 K and reduced at 773 K, (B) calcined at 973 K and reduced at 773 K.
In Figure 6.9 (A), it can be seen that no significant diffraction peaks were detected in the Ni-MnOₓ/SBA-15-C723 and XRD patterns are the same with the fresh catalysts, indicating that there is no effect in the catalysts after steam reforming experiments. Catalytic steam reforming experiments of Ni-MnOₓ/SBA-15-C973 catalysts were conducted after pre-reduction of catalysts at 773 K or 973 K. In 10Ni/SBA-15-C973 (pre-reduced 773 K), diffraction peaks of Ni₀ and NiO were detected and their particle sizes are 10.43 nm and 6.62 nm, respectively. In 10Ni-Mn/SBA-15-C973 (pre-reduced 973 K), metallic Ni diffraction peaks were observed and the crystallite size was slightly larger than that of the corresponding fresh catalyst due to high catalyst reduction temperature. In the case of used 9Ni-1Mn/SBA-15-C973 catalysts, the metal particle sizes are still maintained to its corresponding fresh catalyst in both reduction temperatures (773 and 973 K). Slightly larger in crystallite size of 7Ni-3Mn/SBA-15-C973 was observed after steam reforming experiment.

### Discussion on effect of SMSI in Ni-MnOₓ/SBA-15 catalysts

It have been known that MSI can strongly effect of the nature of active site but also prevent the active metal from agglomeration and suppress carbon deposition. The higher catalyst calcination temperature enhanced metal support interaction to form Ni₂SiO₄ and NiMn₂O₄ phases in the Ni-MnOₓ/SBA-15-C973 catalysts confirmed by XRD measurement. It was known that SMSI can occur bifunctional effect between active metal and metal oxide support, provides separate reaction sites to improve catalytic performance in term of activity and selectivity. Bifunctional effect includes spillover phenomena in which the reactive species migrate from the active metal or support and reacts at the boundary where the supporting oxide provides the second reaction site in the so called “dual site” reaction system. In our prepared catalysts, it was expected that spillover effect enhanced the catalytic activity. Mn addition to Ni metal enhanced the packaging of metal particles into the porous channel of SBA-15 support, MSI, and to form much smaller metal particles. Very SMSI showed negative impact due to encapsulate of active metal species by support material. This effect was more significant in 7Ni-3Mn/SBA-15-C973 catalyst. According to TPR results, reduction pretreatment of the Ni-MnOₓ/SBA-15 catalysts at 773 K was not sufficient to reduce all of the active metal species. However, the catalysts showed high performance which can be expected that hydrogen from decomposition of tars and steam was partially reduced the metal oxide during the steam reforming reaction. This phenomena have been reported in the references.

### Table 6.4. The sizes of the metal particle of used catalysts from XRD measurement

<table>
<thead>
<tr>
<th>Used catalyst</th>
<th>Reduction temperature (K)</th>
<th>D₁₀₀ (nm)</th>
<th>D{subscript}metal particle (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10Ni-C973</td>
<td>773</td>
<td>12.98</td>
<td>8.52*</td>
</tr>
<tr>
<td>9Ni-1Mn; C973</td>
<td>773</td>
<td>12.6</td>
<td>3.29*</td>
</tr>
<tr>
<td>7Ni-3Mn; C973</td>
<td>773</td>
<td>12.6</td>
<td>4.07*</td>
</tr>
<tr>
<td>10Ni; C973</td>
<td>973</td>
<td>12.6</td>
<td>11.79*</td>
</tr>
<tr>
<td>9Ni-1Mn; C973</td>
<td>973</td>
<td>12.6</td>
<td>4.69*</td>
</tr>
</tbody>
</table>

*assuming as Ni₀
*average value of assuming as Ni₀ and NiO

Since 10Ni/SBA-15-C973 and 9Ni-1Mn/SBA-15-C973 catalysts (pre-reduced at 773 K) exhibited the higher performance than the other catalysts in this experiment, comparison with the reported catalysts was considered with them. When assuming as biomass feed rate = 3.3 mg/min (fixed pyrolysis bed: it was estimated that 0.5 g of biomass was decomposed during heating up pyrolysis bed to desired temp. within 15 min), formation rate of combustible gases in 10Ni/SBA-15-C973 and 9Ni-1Mn/SBA-
15-C973 catalysts were 2351 μmol/min and 2246 μmol/min, respectively. These values are higher than the recently developed hydrotalcite-like compound Ni-based CSRT-biomass catalysts.\textsuperscript{6} Volume \% of H\textsubscript{2} in product gas and amount of H\textsubscript{2} formation in 10Ni/SBA-15-C973 were 67.5\% and 60 mmol/g biomass while in 9Ni-1Mn/SBA-15-C973 catalysts have 66.3 \% and 58 mmol/g biomass. These value showed still higher than the references.\textsuperscript{25, 26} Furthermore, the amount of carbon deposition on these two catalysts were negligible and the crystallite size of catalysts after activity experiment still maintained as its fresh catalysts. Therefore, these two factors can be represented as high stable catalysts.

6.4 Conclusion
Synthesise of the Ni-MnO\textsubscript{x}/SBA-15 catalysts by ethylene glycol assisted impregnation technique obtained the catalysts with small particle size and high dispersion into the SBA-15 support. 10Ni/SBA-15-C973 and 9Ni-1Mn/SBA-15-C973 catalyst exhibited higher activity and H\textsubscript{2} yield than 10Ni/SBA-15-C723 and 9Ni-1Mn/SBA-15-C723 catalysts, associating with formation of Ni\textsubscript{2}SiO\textsubscript{4} and NiMn\textsubscript{2}O\textsubscript{4} phases in high temperature calcined catalysts. However, 7Ni-1Mn/SBA-15-C973 catalyst show lower performance than 7Ni-1Mn/SBA-15-C723 due to either partially covering or encapsulation of active metal species by support materials. Higher reduction temperature, 973 K, showed negative impact in the activity of catalysts by aggregation of metal particles. The order in activity of catalyst in term of product gas formation \% was 9Ni-1Mn/SBA-15-C973 > 9Ni-1Mn/SBA-15-C723 = 10Ni/SBA-15-C973 > 10Ni/SBA-16-C723 > 7Ni-3Mn/SBA-15-C723 > 7Ni-3Mn/SBA-15-C973 and the order in H\textsubscript{2} yield was 10Ni/SBA-15-C9673 > 9Ni-1Mn/SBA-15-C973 > 9Ni-1Mn/SBA-15-C723 > 7Ni-3Mn/SBA-15-C973 > 7Ni-3Mn/SBA-15-C723 > 10Ni/SBA-15-C723. According to above results and discussion, the prepared catalysts can be the potentially applicable as tar steam reforming catalyst. But, long time activity test was still required to confirm the life time of the catalysts.

References
1. T.A. Milne, C.C. Elam and R.J. Evans, National Renewable Energy Laboratory (NREL), IEA/H\textsubscript{2}/TR-02/001.
2. E. David, Chemical Engineering Transactions, 2015, 43, 403-408.
CHAPTER 7
CONCLUSION AND RECOMMENDATIONS

7.1 Conclusion

In this study, the catalytic activities of the transition metal catalysts (Co/SiO₂, Fe/SiO₂, and Ni/SiO₂) was firstly investigated in the CSRT-biomass reaction using tubular-flow fixed bed reactor. The effect of metal loading and support were examined on Ni/SiO₂ and Ni/SBA-15 catalysts. The Ni-MnOₓ/SBA-15 catalysts with high resistance to carbon deposition and sintering were obtained by EG assisted impregnation technique and activity experiments were conducted out using a two-stage fixed bed reactor (fixed pyrolysis bed and fixed catalyst bed). Relation between SMSI and catalytic activity of Ni-MnOₓ/SBA-15 was studied to obtain a more superior tar steam reforming catalyst with high activity and high stability.

The findings from this study was concluded as follows:

I. In the examination of tar steam reforming performances of the SiO₂ supported Ni, Co, and Fe catalysts, Ni/SiO₂ catalyst showed the higher performance.

II. In the study of support material effect on Ni catalyst, SBA-15 supported catalysts exhibited higher performance than SiO₂ supported catalysts, associating with high surface area and mesoporous nature of SBA-15 material. Additionally, Ni/SBA-15 catalyst showed lower extend to occur methane formation reaction than Ni/SiO₂ catalyst.

III. 20wt% Ni/SBA-15 catalyst resulted in the higher performance than 10wt% and 30wt% Ni/SBA-15 catalysts. Agglomeration of active metal species was observed in 30wt%Ni/SBA-15 after activity experiment, leading to loss of available active metal site.

IV. Highly dispersed Ni-MnOₓ/SBA-15 catalysts with small particle size (< 5 nm) were obtained by ethylene glycol assisted impregnation technique. 10Ni/SBA-15 catalyst and 9Ni-1Mn/SBA-15 catalyst showed complete tar conversion even at low reaction temperature, 773 K.

V. Addition of small amount (1 wt%) of Mn to Ni further enhanced the product gas formation and H₂ yield. The improved in performance of 9Ni-1MnOₓ/SBA-15 catalyst was due to increased dispersion of Ni NPs by Mn addition, and supply of O₂ from MnOₓ to active Ni species, which promoted the reaction between carbonaceous species and oxygen species on the Ni surface.
VI. Ni-MnO\(_x\)/SBA-15 catalysts calcined at higher temperature, 973 K, increased metal-support interaction to form Ni\(_2\)SiO\(_4\) and NiMn\(_2\)O\(_4\) phases.

VII. 10Ni/SBA-15-C973 and 9Ni-1Mn/SBA-15-C973 catalyst exhibited higher activity and \(\text{H}_2\) formation than 10Ni/SBA-15-C723 and 9Ni-1Mn/SBA-15-C723 catalysts, associating with formation of Ni\(_2\)SiO\(_4\) and NiMn\(_2\)O\(_4\) phases and by effect of spillover in which the reactive species migrate from the active metal or support and reacts at the boundary (Ni\(_2\)SiO\(_4\) and NiMn\(_2\)O\(_4\) phases) where it provides the second reaction site.

VIII. 7Ni-1Mn/SBA-15-C973 catalyst show lower performance than 7Ni-1Mn/SBA-15-C723 due to either partially covering or encapsulation of active metal species by support materials.

IX. Reduction of Ni-MnO\(_x\)/SBA-15 catalysts at higher temperature, 973 K, showed negative impact in the activity due to aggregation of metal particles.

X. The order in activity of catalyst in term of product gas yield was 9Ni-1Mn/SBA-15-C973 > 9Ni-1Mn/SBA-15-C723 = 10Ni/SBA-15-C973 > 10Ni/SBA-16-C723 > 7Ni-3Mn/SBA-15-C723 > 7Ni-3Mn/SBA-15-C973.

XI. The order in \(\text{H}_2\) production amount was 10Ni/SBA-15-C9673 > 9Ni-1Mn/SBA-15-C973 > 9Ni-1Mn/SBA-15-C723 > 7Ni-3Mn/SBA-15-C973 > 7Ni-3Mn/SBA-15-C723 > 10Ni/SBA-15-C723.

XII. Volume % of \(\text{H}_2\) in product gas and amount of \(\text{H}_2\) formation in 10Ni/SBA-15-C973 were 67.5% and 60 mmol/g biomass while in 9Ni-1Mn/SBA-15-C973 catalysts have 66.3 % and 58 mmol/g biomass.

XIII. The highly active Ni/SBA-15 and Ni-MnO\(_x\)/SBA-15 catalysts in tar steam reforming were developed. The catalysts showed high tar conversion, low coke formation and high \(\text{H}_2\) yield even at 773 K steam reforming temperature.

XIV. Two stage fixed-bed (fixed pyrolysis bed and fixed catalyst bed) system was proved as an efficient reaction system to produce the product gas with high \(\text{H}_2\) yield.

According to above results and discussion, the prepared Ni-MnO\(_x\)/SBA-15 catalysts can be the potentially applicable as tar steam reforming catalyst.

7.2 Recommendation

Based on the results of this study, the future work of this study was recommended as follow;

I. Long term stability test was required to observe the life time of catalyst using continuous feeding system of biomass pyrolysis bed.

II. The operating parameters such as steam/carbon ratio, catalyst/ biomass ratio,
feeding rate or flow rate of volatile matters (tar) was need to checked.

III. The applicability of ethylene glycol assisted impregnation technique in preparation of supported metal catalysts with cheaper and easily available support material should investigate.

IV. Although the effect of strong metal-support interaction (SNSI) have been extensively studied in the reducible metal oxide (e.g. TiO$_2$, CeO$_2$) supported transition metal and noble metal catalysts, there are few studies on non-reducible oxide supported (e.g. silica, alumina) catalysts. Therefore, extensive study should explore SMSI effect on non-reducible oxide supported metal catalysts.

V. Reaction mechanism and kinetic of tar steam reforming reaction over Ni-MnO$_x$/SBA-15 catalyst should study.

VI. The applicable of Ni-MnO$_x$/SBA-15 catalysts should test on the other reforming reactions and processes.
LIST OF PUBLICATIONS

Published article in refereed journals


Submitted article in refereed journals


Conference Presentations


Figure A1. Production rate of product gas (A) CO, (B) CH₄, (C) CO₂ and (D) H₂ as a function of reaction time at reaction temperature of 873 K in thermal decomposition and steam reforming.
Figure A2. Production rate of product gas (A) CO, (B) CH₄, (C) CO₂ and (D) H₂ as a function of reaction time at reaction temperature of 873 K in steam reforming over transition metal catalysts.
Figure A3. Production rate of product gas (A) CO, (B) CH₄, (C) CO₂ and (D) H₂ as a function of reaction time at reaction temperature of 873 K in steam reforming over SiO₂ supported and SBA-15 supported Ni catalysts.
Figure A4. Production rate of product gas (A) CO, (B) CH₄, (C) CO₂ and (D) H₂ as a function of reaction time; catalytic steam reforming reaction temperature of 773 K and biomass pyrolysis temperature of 973 K over Ni-MnOₓ/SBA-15 catalysts calcined at 723 K.
Figure A5. Production rate of product gas (A) CO, (B) CH₄, (C) CO₂ and (D) H₂ as a function of reaction time; catalytic steam reforming reaction temperature of 773 K and biomass pyrolysis temperature of 973 K over Ni-MnOₓ/SBA-15 catalysts calcined at 723 K or 973 K.
Figure A6. Production rate of product gas (A) CO, (B) CH₄, (C) CO₂ and (D) H₂ as a function of reaction time; catalytic steam reforming reaction temperature of 773 K and biomass pyrolysis temperature of 973 K over Ni-MnOₓ/SBA-15 catalysts calcined at 973 K and reduced at 773 K or 973 K.