

Development of Ni–Fe bimetallic based catalysts for biomass tar cracking/reforming: Effects of catalyst support and co-fed reactants on tar conversion characteristics



N. Laosiripojana^{a,e,*}, W. Sutthisripok^b, S. Charojrochkul^c, S. Assabumrungrat^d

^a The Joint Graduate School of Energy and Environment, CHE Center for Energy Technology and Environment, King Mongkut's University of Technology Thonburi, Thailand

^b Department of Mining and Materials Engineering, Faculty of Engineering, Prince of Songkla University, Songkhla, Thailand

^c National Metal and Materials Technology Center (MTEC), Pathumthani, Thailand

^d Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Thailand

^e PTT Group Frontier Research Center, PTT Public Company Limited, 555 Vibhavadi Rangsit Road, Chatuchak, Bangkok 10900, Thailand

ARTICLE INFO

Article history:

Received 16 March 2014

Received in revised form 7 June 2014

Accepted 8 June 2014

Available online 27 June 2014

Keywords:

Biomass tar

Cracking

Reforming

Ni–Fe catalyst

Perovskite

ABSTRACT

Catalytic activities of Ni- and Ni–Fe bimetallic based catalysts supported by palygorskite, MgO–Al₂O₃, La_{0.8}Ca_{0.2}CrO₃, and La_{0.8}Ca_{0.2}CrO₃/MgO–Al₂O₃ toward the cracking and reforming of naphthalene and toluene (as biomass tar model compounds) as well as real biomass tar from pyrolysis of eucalyptus wood chips were studied. At 700–900 °C, the main products from the cracking of these hydrocarbons are H₂, CH₄, C₂H₄, C₂H₆, and C₃H₆. Among all catalysts, Ni–Fe supported by MgO–Al₂O₃ and La_{0.8}Ca_{0.2}CrO₃/MgO–Al₂O₃ show the highest H₂ yield values and good resistance toward carbon deposition. Additions of H₂O and CO₂ can promote steam and dry reforming, from which H₂ and CO were the major products from the reaction and the amount of carbon formation was considerably reduced. Importantly, the H₂O/tar and CO₂/tar ratios strongly affect the H₂ yield value, particularly for Ni–Fe/La_{0.8}Ca_{0.2}CrO₃/MgO–Al₂O₃ due to the presence of perovskite-based La_{0.8}Ca_{0.2}CrO₃. At proper H₂O/tar and CO₂/tar ratios, La_{0.8}Ca_{0.2}CrO₃ behaves like the partly-reduced metal-oxide catalysts and promotes the reforming activity. Addition of O₂ along with H₂O and/or CO₂ can further reduce the carbon formation and increase the H₂ yield. Nevertheless, excess O₂ could oxidize metal particles and combusted H₂ to H₂O, which causes lower H₂ yield production.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Nowadays, biomass gasification is known to be one of the promising biomass conversion technologies for heat and power generation as well as chemical production. It is also well established that the main limitation of biomass gasification is to overcome the problem of tar formation in the gaseous product. In general, tar is the complex and high molecular weight compounds containing more than 10,000 species of aromatic. This compound can be easily deposited on the surface of gas engines and results in reducing the engine efficiency as well as increasing the engine maintenance requirement. Therefore, tar removal or conversion into small-molecule gases is strongly required. Among the tar conversion techniques, catalytic cracking and/or reforming has been currently considered as the most promising and effective route [1–4], from which

the main catalysts applied in this process include metallic-based catalysts [5–7], alkali metal-based catalysts [4,8], dolomites and olivine [9–11]. Recently, Ni-, Fe-, and Ni–Fe bimetallic based catalysts supported by several metal oxide materials (e.g. Al₂O₃, MgO, SiO₂, SiO₂–Al₂O₃, MgO–Al₂O₃) have widely been studied and reported to enhance good catalytic performance toward tar and aromatic hydrocarbon decompositions [12–16]. Furthermore, several recent studies have applied palygorskite (PG) as the catalyst support due to its excellent surface and adsorption properties [17–22].

It has been evident that the selection of support material is an important issue as metal catalysts are not very active for the reforming or cracking when supported on inert oxides [23]. Currently, the promising catalyst for the reforming reactions appears to be metals on Al₂O₃, MgO, MgO–Al₂O₃ supports [23–25]. It should be noted that, recently, perovskite-based material with the formula of ABO₃ has also been widely applied as the catalyst and support [26–29]. For instance, LaCrO₃-based perovskite material has been extensively studied as catalyst and support for hydrocarbon reforming reactions due to its high resistance toward carbon formation [28,29]. In addition, it has also been reported that the partial substitution of La at the A-site cation with Ca can improve the

* Corresponding author at: The Joint Graduate School of Energy and Environment, CHE Center for Energy Technology and Environment, King Mongkut's University of Technology Thonburi, Thailand.

E-mail address: navadol@jgsee.kmutt.ac.th (N. Laosiripojana).

stability and catalytic activity of LaCrO_3 toward the steam reforming of hydrocarbons [30–32].

The present work focuses on the synthesis and testing of Ni- and Ni-Fe bimetallic based catalysts supported by several materials i.e. palygorskite, $\text{MgO-Al}_2\text{O}_3$, $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$, and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3/\text{MgO-Al}_2\text{O}_3$ toward the tar decomposition. It is noted that $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3/\text{MgO-Al}_2\text{O}_3$ was synthesized to minimize the weakness of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ on its low surface area properties. Naphthalene and toluene were firstly applied as the tar model compounds for catalyst screening, while real biomass tar was later tested over the optimized catalyst and operating conditions. Naphthalene was chosen since it is one of the most stable products present in tar [33], while toluene was also selected for comparison due to its abundance in tar product [34]. In detail, the stability, activity and product distribution of these synthesized catalysts toward the tar cracking were carried out under selected base condition. Then, the effect of possible inlet co-reactant adding i.e. steam, CO_2 , and O_2 (as partial oxidation and autothermal reforming) on the product distribution was studied and discussed. Importantly, the resistance toward carbon formation and the influence of temperature on the rate of tar conversion and amount of carbon formation were also determined.

2. Experimental

2.1. Raw material

Naphthalene and toluene were applied as the tar model compounds, while the real biomass tar was obtained from the pyrolysis of Eucalyptus (*Eucalyptus grandis*) wood chips obtained from a local pulp mill in Ratchaburi, Thailand. The wood chip composition includes 45% cellulose, 21% hemicelluloses, 30% lignin, and 4% ash. Detail of tar produced from biomass pyrolysis is described in Section 2.3.

2.2. Catalyst preparations and characterizations

Ni (10 wt.% Ni) and Ni-Fe (5 wt.% Ni and 5 wt.% Fe) supported by palygorskite and $\text{MgO-Al}_2\text{O}_3$ were prepared by impregnating commercial grade palygorskite (with the surface area of $220 \text{ m}^2 \text{ g}^{-1}$) and $\text{MgO-Al}_2\text{O}_3$ was synthesized with $\text{Ni}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$. It is noted that $\text{MgO-Al}_2\text{O}_3$ was prepared by impregnating $\gamma\text{-Al}_2\text{O}_3$ with $\text{Mg}(\text{NO}_3)_2$ (the MgO content was 15% by mass). $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ was prepared by precipitation method by mixing 0.1 M of all nitrate precursors (La, Ca, and Cr; from Aldrich) with 0.4 M of ammonium hydroxide at a 2:1 volumetric ratio. Ni-Fe/ $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ was prepared by impregnation of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, while Ni-Fe/ $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3/\text{MgO-Al}_2\text{O}_3$ was prepared by impregnation of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ (20 wt.%) and $\text{MgO-Al}_2\text{O}_3$ (80 wt.%) with $\text{Ni}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$. It is noted that all supports (i.e. $\text{MgO-Al}_2\text{O}_3$, $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3/\text{MgO-Al}_2\text{O}_3$) were calcined at 900°C before impregnating with metal salts. After impregnation, all catalysts were dried at 110°C and calcined again at 900°C . Before the reaction test, the catalysts were characterized by several physicochemical methods i.e. X-ray diffraction (XRD), X-ray fluorescence (XRF), temperature-programmed reduction (TPR) under hydrogen flow, H_2 chemisorption, and BET measurement to determine the phase formation, weight content of metal loading, suitable reducing temperature, metal reducibility and dispersion percentages, and catalyst specific surface areas. From the TPR study as shown in Fig. 1, it can be seen that all catalysts are reduced at the temperature range between 200 and 400°C . Furthermore, the use of $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ as the support seems to decrease the catalyst reducing temperature. Therefore, in the present work, all catalysts were reduced under H_2 flow at 400°C for 6 h before use. It is noted that, after reduction, H_2 chemisorption was applied to determine the metal reducibility and dispersion percentages, from which the metal reducibility was defined from the proportion of hydrogen uptake, while the metal dispersion percentage was calculated from the equation of $N_m SM/100L$ (where N_m is the monolayer of hydrogen uptake, S is the adsorption stoichiometry of

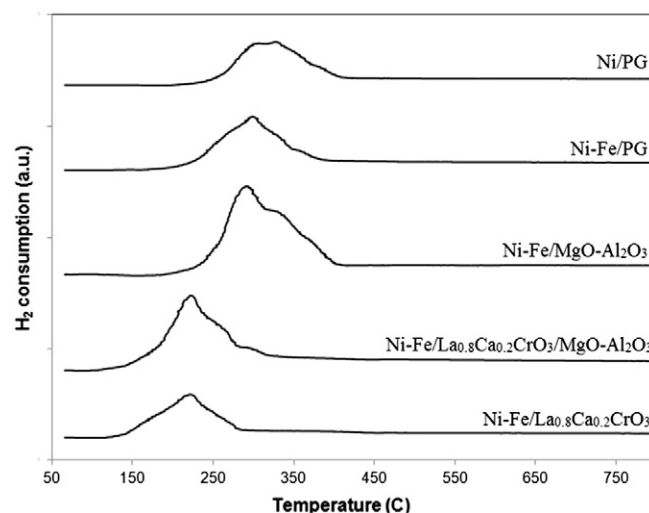


Fig. 1. TPR study of all synthesized catalysts.

H_2 , M is the molecular weight of loading metal, and L is percent metal loading). All physicochemical properties of the synthesized catalysts are given in Table 1.

2.3. Catalytic testing

To undergo the catalytic testing, the system with fixed bed quartz reactor was applied. For the testing over tar model compounds, the feed gases i.e. helium (as carrier gas), O_2 and CO_2 were controlled by three mass flow controllers. Toluene and H_2O were introduced by the heated syringe pumps and vaporized by our designed quartz vaporizer-mixer system, while naphthalene was introduced via the saturator system. All feeds were introduced to a quartz reactor, which is mounted vertically inside tubular furnace. It is noted that a type-K thermocouple covered with small closed-end quartz rod was inserted in the middle of the quartz tube to measure the actual temperature gradient during the reaction. In each experiment, 100 mg of catalyst was used. Prior to the catalyst activity testing, preliminary experiments were performed to determine the suitable experimental conditions where the internal and external mass transfer effects are not predominant. From the studies, the total gas flow rate through the reactor was kept constant at $100 \text{ cm}^3 \text{ min}^{-1}$ under a constant residence time in all experiments to avoid the external mass transfer limitation. The suitable average sizes of catalysts were also verified to confirm that the experiments were carried out within the region of isothermal kinetics. From the verification, the catalyst average particle size was $100\text{--}200 \mu\text{m}$ in all experiments.

To perform the biomass pyrolysis for producing tar, another quartz reactor heated by separate electrical furnace was used. Dried eucalyptus wood chips were packed in quartz reactor and heated to 800°C under helium flow. All gaseous and condensate compounds from the reaction were passed through the catalyst containing reactor. It is noted that all lines connecting between these two reactors were heated at 400°C to prevent the condensation of tar compounds. After the reactions, the exit gas mixture was transferred via trace-heated lines to tar condenser to collect all unconverted tar. The permanent gases were then analyzed by on-line Shimadzu 14B gas chromatograph (GC) with connected thermal conductivity detector (TCD) and flame ionization detector (FID) and a mass spectrometer (MS). The mass spectrometer in which the sampling of the exit gas was done by a quartz capillary and differential pumping was used for the transient and carbon formation experiments, whereas the gas chromatography was applied in order to investigate the steady state condition experiments. In the present work, the catalyst activity was defined in terms of conversion and product distribution. H_2 yield was calculated by hydrogen balance, defined as molar fraction

Download English Version:

<https://daneshyari.com/en/article/209780>

Download Persian Version:

<https://daneshyari.com/article/209780>

[Daneshyari.com](https://daneshyari.com)