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Enhanced hydrogen production from catalytic biomass gasification with *in-situ* CO₂ capture

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Abstract: In order to cope with the global energy crisis and environmental pollution problems, there are urgent needs for clean energy such as biomass-derived hydrogen. Porous CaO is effective to promote hydrogen production from biomass gasification due to its high capacity of *in-situ* CO₂ capture. In this work, a two-stage fixed bed was used to produce hydrogen by catalytic pyrolysis of biomass with and without *in-situ* CO₂ capture sorbent. Besides, three Ni loadings (5 wt.%, 10 wt.%, and 20 wt.%) supported by Al₂O₃ and sol-gel CaO have been prepared and tested. The BET analysis showed the surface area of the catalysts increase first and then decrease upon increment in Ni loading. The high-resolution transmission electron microscopy (HRTEM) images revealed the distribution of NiO particles over the porous CaO. The X-ray diffraction (XRD) analyses indicated the NiO nanocrystalline size increased with increasing Ni loading of Ni/Al₂O₃, and the most homogeneous dispersion was shown by 10 wt.% Ni/CaO. Around 666 mg_{CO2}/g_{CaO} of CO₂ adsorption capacity and 850 min stability were obtained using the sol-gel CaO sorbent. Compared with reference Ni/Al₂O₃ catalysts, the resistance of carbon deposition of Ni/CaO results in lower coke deposition, which is attributed to an increase of the basicity of catalysts with the presence of alkaline-earth element. Enhanced catalytic function by increasing Ni loading promoted the decomposition of biomass-derived oxygenated compounds. Much more hydrogen was obtained using the Ni/CaO catalysts compared to Ni/Al₂O₃ due to *in-situ* CO₂ capture. However, sintering and particle agglomeration caused by Ni loading as high as 20 wt.% reduced hydrogen production. The highest H₂ concentration of 19.32 vol.% at 424 °C was obtained when the 10 wt.% Ni/CaO catalyst was used.

Keywords: Biomass gasification, Hydrogen production, *in-situ* CO₂ capture.

1. Introduction

The consequences of over-exploitation and the consumption of fossil fuels cause significant climate changes and environmental pollution(Cheng et al., 2020). Therefore, the development of more efficient and clean renewable energy sources is urgently needed to solve these problems. Hydrogen has been recognized as one promising clean energy carriers for a sustainable energy system, and it can be produced via several ways including solar water splitting, methane dry reforming and steam reforming technique(Akbari-Emadabadi et al., 2017; Cheng et al., 2019; Chong et al., 2019a; Suzuki et al., 2019). Since most of hydrogen is currently produced from the fossil fuel source, converting the largely available and carbon-neutral renewable feedstock, such as biomass, into hydrogen has attracted great attention(Kalinci et al., 2009; Kumagai et al., 2015; Srirangan et al., 2012).

Globally, 170 billion metric tons of biomass sources are produced(Ma et al., 2019). At the meantime, Biomass wastes from agriculture, forestry and wood processing industries are largely produced and the disposal and management of these wastes become more challenging(Cho et al., 2020). The wood of fir is one of the widespread and abundant species, and it is often used as structure timbers and manufacturing plywood, which generate large amount of sawdust and wood residues(Kazemi et al., 2016). As shown in Eq. (1), thermochemical decomposition of biomass under inert atmosphere (pyrolysis) produces H_2 , CH_4 , CO , CO_2 , tar and char(Duan and Yu, 2018; Widyawati et al., 2011). It is noted that due to the presence of moisture in biomass, gasification also happens during biomass pyrolysis.

Transition metal oxide and noble metal catalysts have been applied to produce hydrogen during

biomass pyrolysis/gasification(Azimi et al., 2019; Diaz-Rey et al., 2015; Duman et al., 2014; Huang et al., 2012; Isha and Williams, 2016). Ni-based catalysts are effective for cleavage of C-H, C-C and O-H bonds of biomass-derived oxygenated compounds to H₂, CO and CO₂ at the high reaction temperature(Fermoso et al., 2012a; Micheli et al., 2017; Wu et al., 2011). Besides, the noble catalysts, such as Rh(Tomishige et al., 2004) (Lemonidou et al., 2013) and Ru(Chiodo et al., 2010), had been found better performance than the commercial Ni catalyst. However, the challenge in implementing these catalysts for hydrogen production is the high cost associated with the catalyst formulations, which features prohibitively high noble metal loadings (typically ranging from 5 to 15 wt.%(Dou et al., 2019). Ni-based catalyst seems to provide a prerequisite for large-scale industrial applications.

In addition, the thermal conversion of biomass needs for a catalyst with resistance against coke formation, high stability and antisintering property. For this case, some mesoporous supports such as nano silica, KCC1 and DFSBA-15 had been achieved to provided high surface areas for metal dispersion and to minimize clogging(Chong et al., 2019a). In addition to be a catalyst support, the *in-situ* CO₂ adsorption function of porous CaO (Eq. (2)) during biomass pyrolysis/gasification has been considered a promising pathway to improve the quality of syngas via enhanced water-gas shift reaction (WGSR) (Eq. (3)). Researches about bifunctional materials combining metal catalyst and CaO promoting H₂-rich syngas from biomass in recent years have been listed in Table S1.

However, the features of CaO-sorbent such as easily sintering, particle size and instability are

key factors affecting the conversion efficiency and useful life problems. The modification of CaO, as well as nanostructured CaO-based sorbents can improve the limitation of sintering and CO₂ adsorption capacity of CaO. Therefore, based on the roles of bifunctional catalysts, it is of interest to study the relationship between the CO₂ adsorption using a nano-CaO sorbent and to obtain an excellent target product from biomass.

The aim of the work is to investigate the enhanced effect using dual functional materials (Ni/CaO) on hydrogen production from gasification of real biomass. In particular, a sol-gel method was used to prepare the CaO as the catalyst support to enhance CO₂ capture ascribed to its porous structure compared to commercial CaO. In addition, Ni/Al₂O₃ catalysts were used without CO₂ capture during biomass gasification to facilitate the understanding of the performance of Ni/CaO dual functional catalysts. It is noted that the regeneration of Ni/CaO dual functional materials is not studied in this work. Its regeneration could be integrated with CO₂ conversion by introducing hydrogen.

2. Materials and methods

2.1 Materials

Sawdust of fir, with a particle size of around 1 mm, was used as a representative biomass feedstock in this study. The elemental and proximate analysis of the biomass samples is shown in Table 1.

Table 1. Elemental and proximate analysis of the wood biomass

Elemental analysis (wt.%)	C	H	N	S	O ^a
	47.75	5.61	1.96	0.10	44.58
Proximate analysis (wt.%)	Moisture	Volatiles	Fixed carbon	ash	
	12.8	67.1	14.2	5.9	

a. Calculated by difference.

Sol-gel CaO and Al₂O₃ (Sigma-Aldrich, 99.99%) were used as catalyst supports. The CaO sorbent used in this work was synthesized with a standard sol-gel route proposed by Sun et al. (Sun et al., 2019). A certain amount of calcium nitrate tetrahydrate (Sigma-Aldrich, 99.99%) and citric acid (Sigma-Aldrich, 99.99%) were dissolved in deionized water successively at room temperature. The mixture was continuously stirred at 80 °C to form a sol. It was dried overnight at 130 °C followed by calcination at 850 °C for 5 h with a 2 °C min⁻¹ heating rate.

Three percentages of Ni supported catalysts (5 wt.%, 10 wt.%, and 20 wt.%) were prepared. The predetermined amount of Ni(NO₃)₂·6H₂O was added into the dissolved sol-gel CaO and Al₂O₃ (Sigma-Aldrich, 99.99%) solutions, respectively. The mixture was dried at 80 °C for around 12 h, followed by calcination in a muffle furnace at 750 °C for 6 h with the heating rate of 2 °C min⁻¹. After that, the calcined catalysts were grounded and sieved to collect particles with sizes between 165 and 350 μm.

2.2 Characterization of catalysts

X-ray diffraction (XRD, AXS D8 Advanced using CuKα radiation with 0.1542 nm wavelength, BRUKER) of the catalysts were performed to identify the crystalline phases. The data was collected in the 10-80° 2θ range. The diffraction spectra have been indexed by comparison with the joint committee on powder diffraction standards (JCPDS) files. The crystallite size of different crystalline phases was determined by Debye–Scherrer’s equation from the width at half-height (FWMH) of the more intense and better deconvoluted ray of each phase.

Temperature programmed reduction (TPR) was performed to characterize the fresh catalysts in a thermo-gravimetric analyzer (TGA, SDT Q600). Around 10 mg of fresh catalyst was placed in the crucible which was heated up to 700 °C with a heating rate at 3 °C min⁻¹ in a reduction

atmosphere (5% hydrogen and 95% nitrogen).
BET and BJH methods were applied on N₂ adsorption-desorption measurement at 77K using an automatic adsorption equipment (ASAP2020, Micromeritics) to determine the specific surface area and the values of pore volume and pore size. A scanning electron microscopy (SEM, MERLIN compact, ZEISS) and high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F20, FEI, USA) with accelerating voltage of 10 kV were utilized to observe the morphology of the fresh catalysts and the surfaces morphology of used catalysts.
Carbon formation on the surface of the used catalysts was tested by temperature-programmed oxidation (TPO) in TGA. Around 10 mg of the used catalyst was placed on an alumina balance and heated to 800 °C and hold for 10 min with a heating rate of 15 °C min⁻¹ at the atmosphere pressure.

2.3 Sorption properties

2.3.1 Sorbent capacity for CO₂ capture

5 to 10 mg of prepared CaO adsorbent and catalyst/sorbent materials were tested for adsorption capacity. The materials were first raised to 800 °C at a rate of 10 °C min⁻¹ in a nitrogen atmosphere (100 mL min⁻¹) using TGA, in order to remove moisture and carbon dioxide in the sample. Then it was cooled down to 700 °C for CO₂ sorption. After reaching the target temperature, the inlet gas was switched to 15% CO₂ balanced with 85% N₂ for adsorption for 90 min. Then gas atmosphere was switched to pure nitrogen for 30 min at the same temperature and then was temperature programmed to 800 °C with 5 °C min⁻¹ to completely eliminate carbon dioxide.

2.3.2 Stability of sorbent for carbonation/Calcination test

In order to investigate the stability of CO₂ capture of the CaO sorbent during the biomass pyrolysis process, the carbonation and calcination of the developed CaO sorbent was tested using TGA. Around 5 mg fresh CaO sorbent was put into the TGA chamber. The conditions mentioned earlier for the sorbent capacity test were used during this stability test and the whole test was 850 min. The carbonation conversion of each cycle was calculated as equation (Eq. (4))(Sun et al., 2019):

$$C \text{ (\%)} = \frac{m_t - m_c}{m_c} \frac{M_{CaO}}{M_{CO_2}} 100\% \quad \text{Eq. (4)}$$

Where C means the conversion of the carbonation, m_t and m_c stand for CaO undergo carbonation for t min and after calcination, and M_{CaO} and M_{CO_2} are the mole masses of CaO and CO₂, respectively.

2.4 Pyrolysis of biomass using a two-stage reactor

Fig. 1. Schematic diagram of the two-stage pyrolysis reactor system

The experiments were carried out using a two-stage reactor shown in Fig. 1. The pyrolysis of biomass was conducted in the first stage and the gas production was catalytic reforming in the second stage. During the experiment, 0.5 g catalyst was placed in the second stage and heated to 700 °C with the rate of 35 °C min⁻¹ and stabilized until the end of the experiment. When the second stage reached the target temperature, the first stage containing 2 g of fir sawdust was programmed to 500 °C at a heating rate of 20 °C min⁻¹ and hold for 20 min. The entire process was carried out under inert nitrogen (100 mL min⁻¹) atmosphere. The condensable products were collected by dry ice and the non-condensable gases were analyzed by an on-line gas detector (MAC100, ETG).

3 Results and discussion

3.1 Characterization of fresh catalysts

3.1.1 BET of the fresh catalysts

N₂ adsorption-desorption isotherms and pore size distributions of samples are explicated in Fig. S1. The textural properties of different metal loading materials are summarized in Table 2. According to the IUPAC classification, the characteristic of adsorbents is compatible with the type IV isotherm and H4-typed hysteresis loop (Fig. S1(a)). It is indicated the formation of mesoporous Ni/CaO materials. 5 wt.% Ni/CaO and 10 wt.% Ni/CaO have similar mesopore distributions as shown in Fig. S1(b). The highest specific surface area of 138.34 m²g⁻¹ is obtained for 10 wt.% Ni/CaO. It is worth noting that a significant decrease of specific surface area is observed with the 20 wt.% Ni loading on Ni/CaO. This might be due to micropores blockage of metal oxide particles. Compared to the Ni/CaO materials, the 10 wt.% Ni/Al₂O₃ catalyst has the largest average pore size of 11.22 nm and the lower specific surface area resulted by the larger average pore size. In addition, the Ni/Al₂O₃ catalysts with different Ni loadings show similar characteristics. This is further supported by the H₂-typed hysteresis loop (Fig. S1(c)), indicating the uniform pore size distribution of the materials.

Table 2. Textural properties of catalysts and the NiO crystallite size calculated by Scherrer equation.

Catalysts	Specific surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore size (nm)	Average NiO Particle size (nm)
5 wt.% Ni/CaO	137.40	0.223	6.51	46.3
10 wt.% Ni/CaO	138.34	0.215	6.23	38.1
20 wt.% Ni/CaO	81.09	0.135	6.67	51.7
5 wt.% Ni/Al ₂ O ₃	79.11	0.216	10.93	50.1
10 wt.% Ni/Al ₂ O ₃	79.71	0.224	11.22	88.4

20 wt.% Ni/Al ₂ O ₃	78.91	0.206	10.45	>100
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3.1.2 XRD analysis of fresh catalysts

XRD patterns of Ni/CaO catalysts are illustrated in Fig. 2(a). The XRD peaks around 32.19°, 37.34°, 53.84°, 64.13°, 67.35° and 79.63° correspond to the (111), (200), (220), (311), (222) and (400) of CaO (PDF card: #77-2010), respectively. The diffraction peak at 2θ=43.2° indicate the presence of (202) lattice plane of cubic NiO, and the intensity of this peak is enhanced with the increase of Ni loading. A weak intensity for the diffraction peaks at 2θ= 29.4° (calcite (104)) and 34.06° (portlandite (101)) can be observed, which suggested the CaCO₃ residue of incompletely calcined catalyst and the reaction with the moisture from the air, respectively. The results of NiO particle size calculated from the Scherrer's equation are included in Table 2. The smallest particle size (38.1 nm) of NiO is obtained in 10 wt.% Ni/CaO indicating a better particles dispersion. According to the literature (Carrero et al., 2010; Wu et al., 2011), the smaller size of the catalyst could contribute to a high catalytic activity. The XRD spectra of Ni/Al₂O₃ is shown in Fig. 2(b). The characteristic peaks of Al₂O₃ (2θ=19.5°, 31.9°, 45.8°, and 66.7°) and NiO (2θ= 62.9°) indicate the presence of support and catalyst within the materials (Teo et al., 2019). It is worth pointing out that strong nickel spinel phase (2θ=37.4°) was generated during catalyst preparation because of the interaction between metal and support. With the increasing Ni loading, larger NiO nanocrystalline size can be detected on Ni/Al₂O₃, which is attributed to the crystal agglomeration with the high amount Ni loading (Chong et al., 2019b).

Fig. 2. X-ray diffractograms of the fresh catalyst: (a) Ni/CaO, (b) Ni/Al₂O₃

3.1.3 TPR results of fresh catalysts

DTG-TPR were conducted to identify the metal species under different temperatures. It can be obviously observed that there are two reduction peaks for the Ni/CaO sample (Fig. S2(a)). The peak around 390 °C can be assigned to the reduction of bulky NiO particles to Ni. The highest peak at this temperature of 10 wt.% Ni/CaO shows the presence of a large amount of bulky NiO particles on the surface of the sample. The peak above 600 °C is related to the reduction of NiO species which have high interaction with CaO sorbent(Valle et al., 2014; Yao et al., 2017). The corresponding peak for 10 wt.% Ni/CaO catalyst has a relatively lower intensity compared to the other calcium support catalyst, suggesting a weaker interaction between NiO and the CaO sorbent. This is consistent with the particle size calculation from XRD analysis (Fig. 2(a)). Compared with Ni/CaO, the TPR results of Ni/Al₂O₃ are quite different (Fig. S2(b)). There are no obviously reduction peaks for 5 wt.% and 10 wt.% Ni/Al₂O₃. It is assigned to reduction of NiAl₂O₄ which was resulted from a very strong interaction between nickel and Al₂O₃. This can be further confirmed by the XRD results (Fig. 2(b))(Alipour et al., 2014b; Roh and Jun, 2008; Valle et al., 2014). In contrast, the presence of bulky NiO is observed for the 20 wt.% Ni/Al₂O₃

catalyst with obvious reduction peaks at around 450 °C and 550 °C, which is attributed to the high Ni loading.

3.1.4 SEM results of fresh catalysts

The SEM images representing the synthesized Ni/CaO materials are shown in Fig. S3. The pristine CaO sorbent has a characteristic of the smooth external surface and homogeneous porous structure (Fig. S3(a)). This could facilitate the accessibility and permeability of reactant gaseous molecules within the sorbent material during biomass pyrolysis/gasification. Uniformly dispersed grain-like particles can be observed, and Ni particles are also uniformly deposited on the surface of sorbent when 5 wt.% Ni was loaded on CaO (Fig. S3(b)). In addition, it seems that the 10 wt.% Ni/CaO catalyst has a well-developed grain structure compared with 20 wt.% Ni/CaO catalyst (Fig. S3(c)(d)). A small particle size of NiO is related to better metal dispersion and was reported to enhance catalytic reaction (Teo et al., 2019).

3.1.5 TEM analysis of fresh catalysts

Fig. 3 shows fine structures of the prepared Ni/CaO nanoparticles. NiO particles can be clearly observed on the surface of the Ni/CaO with the increase of the Ni loading rate. The statistic of the NiO particle size shows that a wider range of particles size can be observed on the higher Ni loading Ni/CaO materials, which is suggested to the low separation and agglomeration of the catalysts. Most particles size with around 40 nm (graph inserted in Fig. 3(b)) and more than 50 nm (graph inserted in Fig. 3(c)) can be found on the surface of 10 wt.% Ni/CaO and 20 wt.% Ni/CaO, respectively, which is consistent with the results of XRD analysis.

Fig. 3. TEM images of the fresh Ni/CaO: (a) 5 wt.%, (b) 10 wt.%, and (c) 20 wt.%

3.1.6 Sorption capacity and carbonation/calcination test

The adsorption-desorption results as well as carbonation/calcination test of the prepared samples are illustrated in Fig. 4. Around $666 \text{ mg}_{\text{CO}_2}/\text{g}_{\text{CaO}}$ of CO_2 adsorption capacity is obtained when the pure CaO was tested. With the increase of Ni loading, the CO_2 adsorption capacity is decreased to 410, 327, and 211 $\text{mg}_{\text{CO}_2}/\text{g}_{\text{Ni/CaO}}$ for 5 wt.%, 10 wt.% and 20 wt.% Ni/CaO, respectively. From the derivative weight graph inserted in Fig. 4(a), the first peaks at around 700°C indicates a fast reaction between CaO and CO_2 to generate CaCO_3 . This corresponds to the first stage of the carbonation of CaO (Sun et al., 2019). When the temperature was held at 700°C for 80 min (From 80 min to around 160 min), the shown platform is attributed to the CO_2 diffuse through CaCO_3 layer to react with inner CaO particles. This process is the slow stage of CO_2 adsorption. The inverted peak at the time of around 720°C suggests the fast decomposition of CaCO_3 . However, compared to the pure CaO sample, the loading of Ni delayed CaCO_3 decomposition.

Six carbonation/calcination cycles of the prepared sol-gel CaO was carried out and exhibits stable CO_2 capture and regeneration of the sorbent sample (Fig. 4(b)). The carbonation conversion calculated by Eq. 4 reduced slightly from 80.59% of the first cycle to 72.42% after

reacted for 850 min. This decay of carbonation conversion over repeated cycles is attributed to the agglomeration and sintering of unsupported CaO and the carbon deposition of the catalyst (Sun et al., 2019).

(a)

(b)

Fig. 4. Capacity tests of the CaO sorbent and Ni/CaO sample: (a) and carbonation/calcination test: (b)

3.2 The effect of the Ni/CaO and Ni/Al₂O₃ on the products yield and composition

3.2.1 Mass balance and product yield

Table 3. Product yields from the pyrolysis of wood biomass

Catalyst/support	Solid residue ^a (wt.%)	Liquid product (wt.%)	Gases (wt.%)
5 wt.% Ni/CaO	17.19	4.41	78.40
10 wt.% Ni/CaO	16.88	5.06	78.06
20 wt.% Ni/CaO	18.51	4.90	76.60
5 wt.% Ni/Al ₂ O ₃	22.20	6.26	71.54
10 wt.% Ni/Al ₂ O ₃	22.86	5.25	71.90
20 wt.% Ni/Al ₂ O ₃	22.26	6.23	71.52

a. including biomass solid residue and the deposited carbon

The experimental results using different catalysts for hydrogen production from catalytic thermal chemical conversion of biomass are shown in Table 3. When 5 wt.% and 20 wt.% Ni/Al₂O₃ are used, the distribution of the obtained products is almost the same. This might be ascribed to their similar material properties as shown in BET results. In contrast, when 10 wt.% Ni/Al₂O₃ used, less liquid products (5.25 wt.%), more solid (22.86 wt.%) and gaseous (71.90 wt.%) products were obtained. Compared to the Ni/Al₂O₃ catalyst, much more gas products and less liquid and solid carbon deposits are obtained by the Ni/CaO materials. The carbon deposition of CaO support materials are obviously decreased as the addition of CaO improved the coke resistance compared with Ni/Al₂O₃. This may be related to an increase of basicity of the catalysts by the presence alkaline-earth elements (Alipour et al., 2014a; Carrero et al., 2010). In particularly, only 16.88 wt.% of carbon residue is obtained when 10 wt.% Ni/CaO was used. The content of each gas product is presented in Fig. 5. It is indicated that biomass-derived gases were evolved at around 20 min after the experiment started, which corresponds to 300 °C (Fig. 5(a)). With the increase of Ni loading from 5 wt.% to 10 wt.%, gas release temperature is reduced (Fig. 5(b)). More Nickel loading is believed beneficial for the probability of biomass-

derived oxygenated compounds conversion (Fermoso et al., 2012a; Micheli et al., 2017). The highest hydrogen concentration of 4.46 Vol.% was detected at 425 °C. However, the production of the gas is almost unchanged compared to 5 wt.% Ni/Al₂O₃, as the 20 wt.% Ni catalyst has relative lower specific surface area, pore volume and average pore. In contrast, the increase of Ni loading on CaO results in the decrease of hydrocarbons from 57 vol.% to 36 vol.% and the increase of hydrogen. Particularly, the highest H₂ concentration of 19.32 vol.% at 25 min (around 424 °C) was detected when the 10 wt.% Ni/CaO catalyst was used. At the same temperature, the hydrogen production of 5 wt.% Ni/CaO and 20 wt.% Ni/CaO are 12.61 vol.% and 14.48 vol.%, respectively (Fig. 5(d)(e)(f)).

During the pyrolysis/gasification of biomass, the hydrocarbons derived from biomass pyrolysis were cracked into low molecular products, such as CO, CO₂, CH₄ and H₂ (Li et al., 2001). Compared to Ni/Al₂O₃ catalysts, the better performance of hydrogen production with Ni/CaO catalysts during biomass catalytic pyrolysis is partly due to the adsorption of CO₂. According to Le Chatelier's principle that the reduction of CO₂ by CaO adsorption helps to shift the equilibrium of multi-carbon volatile gas decomposing towards H₂ (Fermoso et al., 2012b). The Ni-doping on the CaO will decrease the C-O bond stability especially near the Ni atom and be in favor of the CO₂ adsorption capability as well as the decarbonization capacity of Ni/CaO (Zhao et al., 2019). This may be the reason more hydrogen and less carbon deposition were detected when Ni loading was increased from 5 wt.% to 20 wt.% Ni/CaO. Furthermore, moisture derived from the wood sawdust at relatively low temperature also promoted hydrogen production through water-gas shift reaction (eq. (3)) at the beginning of the experiment. Therefore, more hydrogen is obtained using CaO support than Al₂O₃ support.

Overall, the Ni loading is a determining factor for hydrogen production from thermal chemical conversion of biomass. Thus, much more hydrogen is obtained when 10 wt.% and 20 wt.% loading catalysts were used compared to 5 wt.% Ni-based catalysts. However, as the Ni loading increased from 10 wt.% to 20 wt.%, there is slight change of hydrogen production although hydrocarbons decomposition was enhanced. This may be the reason that more carbon was deposited on the used 20 wt.% Ni/CaO as shown in Table 3. Therefore, 10 wt.% Ni is the optimum loading to produce maximum hydrogen in this work. Lower Ni loading (5 wt.%) provides insufficient catalytic Ni sites to catalytic reforming of pyrolysis vapors, while too high Ni loading (20 wt.%) reduces the content of CaO which could largely enhance hydrogen production through sorption enhanced effect.

Fig. 5. On-line analysis of gases from pyrolysis of wood sawdust with different ratio Ni/Al₂O₃: (a) 5 wt.%; (b) 10 wt.%; (c) 20 wt.%; Ni/CaO: (d) 5 wt.%; (e) 10 wt.%; (f) 20 wt.%

3.2.2 Characterization of the used catalysts

XRD results of the used Ni/CaO catalysts are shown in Fig. S4. The peaks of calcium hydroxide were disappeared due to its decomposition during thermochemical conversion of biomass at high temperature. The obvious difference between the fresh and used Ni/CaO catalysts is that there are apparently nickel crystal phases showing at $2\theta=44.6^\circ$, indicating that nickel oxide has

been reduced to nickel during the pyrolysis reforming process. Due to the lower loading of Ni, weak Ni peaks are observed in the 5 wt.% Ni/CaO catalyst.

Fig. 6 shows fine structures of the used Ni/CaO nanoparticles from TEM analysis. Different types of carbons can be found on the used catalysts, and some Ni particles were surrounded by carbon nanotubes (CNTs) with diameter of around 20 nm, especially on the 5 wt.% Ni/CaO catalyst. This indicates that the fine Ni particles reduced from NiO promoted the formation of CNTs. However, larger size grains (>100 nm) were detected in the used 20 wt.% Ni/CaO catalyst compared to the fresh one. It is indicated that excessive metal loading could lead to metal sintering during hydrogen production from biomass (Fig. 6(c)). It is worth noting metal particle sizes are similar for the fresh and used 10 wt.% Ni/CaO catalysts. This might be due to the high dispersion of catalytic sites on the CaO support.

Fig. 6. TEM images of the used Ni/CaO catalysts: (a) 5 wt.%, (b) 10 wt.%, (c) 20 wt.%

The used catalysts had been tested in relation to the carbon deposition using TGA-TPO and the results are shown in Fig. 7. The used Ni/Al₂O₃ (Fig. 7(a)(b)) have more weight loss of the 10 wt.% Ni catalyst than the other two Ni loadings, which indicated more carbons deposited on the material surface. The decomposition temperature of these carbons hints much more amorphous carbon deposited on the Ni/Al₂O₃ catalysts. However, for the used Ni/CaO catalyst,

the majority of deposited carbons are oxidized after 550 °C. It is suggested that the carbon on the used Ni/CaO catalyst is mainly CNTs (Acomb et al., 2015; Yang et al., 2015). For the Ni/CaO catalysts, a weight increase is observed from 100 °C to around 600 °C. This is resulted from the oxidation of nickel and amorphous carbon deposition on the surface of the used catalysts. CaCO_3 is decomposed to CaO and CO_2 after 700 °C causing the weight loss (Fig. 7(c)). In addition, the least weight loss of the used 20 wt.% Ni/CaO is observed indicating that less filament carbons such as CNTs are formed or/and less CaCO_3 is present. The peak at temperature 350 °C and the exothermic peak at temperature 425 °C related to 5 wt.% Ni/CaO in the DTG-TPO graph indicate the oxidation of bulky nickel, respectively. However, the strong metal-support interaction within 20 wt.% Ni/CaO made this process more difficult, so the oxidation temperature increases to 500 °C (Fig. 7(d)). Strong metal-support interaction could inhibit the growth of CNTs (Acomb et al., 2016). This is supported by that metal particles in TEM (Fig. 6(c)) are large which is undesirable for CNTs formation.

Fig. 7. TPO test of the used catalyst: (a)(c) TGA-TPO; (b)(d) DTG-TPO

4 Conclusions

In this paper, hydrogen was produced with and without CO₂ enhanced sorption at different Ni loadings in the catalytic thermochemical conversion of biomass. In conclusion, sol-gel CaO sorbent in the experiment has around 666 mgCO₂/gCaO of CO₂ adsorption capacity. Similar product yields are obtained for Ni/Al₂O₃ catalysts with different Ni loadings due to their almost same textural properties. Much more hydrogen was produced using Ni/CaO catalysts compared to Ni/Al₂O₃ because of *in-situ* CO₂ adsorption. The Ni-doping is in favor of the CO₂ adsorption ability as well as the decarbonization capacity of Ni/CaO materials. It results in a significant decrease of the hydrocarbon production (from 57 vol.% to 36 vol.%) with the Ni loading rate from 5 wt.% to 20 wt.%. Especially, the ability of coke resistance helps the 10 wt.% Ni/CaO to obtain a minimum solids residue of 16.88 wt.%. Compare to the amorphous carbon on the used Ni/Al₂O₃, more CNTs are obtained on the surface of the used Ni/CaO catalyst. However, metal sintering and agglomeration resulted from high Ni loading of 20 wt.% lead to larger metal oxide particles, which is undesirable for hydrogen and CNTs formation. In view of increasing the catalytic activity and improving the adsorption capacity as well as resistance against coke

formation of the sorbent, 10 wt.% Ni/CaO is the optimal catalyst with the highest H₂ concentration of 19.32 vol.% at around 424 °C in this work.

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