

Development of Fe-promoted Ni-Al catalyst for hydrogen production from gasification of wood sawdust

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ABSTRACT:

The production of renewable hydrogen enriched gas from biomass waste is a promising technology for the development of a sustainable economy and society. Until now, there are still challenges of the technology in terms of the efficiency of hydrogen production. Catalyst is known and has been tested to enhance hydrogen production from biomass gasification. In particular using Ni-based catalysts, which have high reactivity for hydrogen production and are cost effective. However, developing a Ni-based catalyst with high thermal stability and resistance of coke deposition on the surface of the catalyst is still a challenging topic. In this work, Ni-Al catalysts doped with low-cost Fe metal were investigated for hydrogen enriched syngas production from gasification of biomass using a two-stage fixed bed reactor. NiO-Fe₂O₃-Al₂O₃ catalysts with various Ni:Fe molar ratios (9:1, 8:2, 6:4, 5:5, 4:6, 2:8 and 1:9) were studied aiming to understand the influence of Fe addition on the production of hydrogen and the catalyst stability in terms of coke deposition on surface. X-ray diffraction (XRD), temperature programme reduction (TPR) and Transmission electron microscopy (TEM) analysis of the fresh catalysts showed that nanoparticles (mainly NiAl₂O₄ spinel phase and Al₂O₃, ~5 nm) were identified in the catalysts. High dispersion of metal particles was obtained using a co-precipitation method of catalyst preparation. With the increase of Fe addition, hydrogen production was reduced from around 11 to 8 (mmol H₂ g⁻¹ biomass). However, the addition of Fe into the Ni-based catalyst significantly reduced the amount of coke deposited on the surface of the catalyst. H₂/CO molar ratio was maximized to 1.28 when Ni:Fe molar ratio was 1:1. In addition, sintering of metal particles was not observed through the TEM analysis of the fresh and reacted catalyst.

1. Introduction

At present, fossil-based fuels, such as petroleum, coal, and natural gas, are used for over three quarters of the primary energy consumption in the world¹. Due to the depletion of resources and the release of greenhouse gases, significant concerns have been raised on the utilization of fossil fuels in regard to energy security and environmental impacts². The development of renewable and clean alternative energy sources is, therefore, deemed to be vital to address the current increasing demand for energy and to decrease environmental impacts of energy consumption^{3, 4}. Currently, alternatives to fossil fuels are renewable fuels, i.e. biomass, hydropower and solar energy⁵. Biomass has attracted increasing attention since it is renewable, carbon neutral, and a wide range of cheap and non-food feedstocks are available.

Hydrogen-enriched syngas production from biomass via the gasification process is a promising technology⁶. Also, hydrogen is an ideal clean fuel source for low carbon energy systems^{7, 8} and can be used directly in fuel cells⁶. Hydrogen has also been identified as an ideal energy carrier for other resources, such as hydropower, wind, solar and biomass^{2, 9}. For example, the electricity generated from wind and hydropower can be converted into hydrogen through electrolysis in the purpose of energy storage. Furthermore, hydrogen-rich syngas production from biomass would result in the decrease of dependence on energy production from fossil fuels and, simultaneously, in the reduction of greenhouse gas emissions¹⁰.

Hydrogen-rich syngas production from biomass gasification receives extensive attention from both industrial and academic researchers due to the high conversion efficiency^{6, 11}. A challenge towards H₂ production from biomass gasification on a large scale is the formation of coke and tar which can be eliminated by thermal cracking (gasification at high temperature) or by the utilization of a catalyst (catalytic gasification)⁶. Particularly, in the presence of steam and catalyst, gas and hydrogen yields can be significantly enhanced because of the promotion of steam reforming and water-gas shift reactions⁶.

It is known that Ni is an excellent element for steam gasification reactions and preferred as a catalytic active site than precious metal such as Pt, Rh and Ru, as Ni-based catalysts are relatively cheap and have high catalytic activities for hydrogen production^{12, 13}. A number of catalyst supports (e.g. MCM-41, Mg-Al and Cu-Al)^{2, 4, 14-16} have been tested for biomass gasification. Among them, Al₂O₃ is regarded as an effective support, in particular, in terms of the catalytic activity for hydrogen production and thermal stability^{17, 18}. It has been reported that the addition of CeO₂ to Ni-catalysts enhanced the catalytic performance, and the formation of the Ni-CeO₂ nanocomposite was responsible for the high catalytic activity and high

resistance to coke formation^{12, 18-20}. However, the cost of Ce species is quite high. It is proposed that Fe species have similar high redox properties as Ce-species and can help promote hydrogen production in the steam gasification of biomass²¹. The addition of Fe in the catalyst can significantly influence the gasification efficiency^{6, 22-25}. For example, it was reported that Fe species promoted water-gas shift, reforming and decomposition reactions during the steam gasification of biomass^{6, 21}.

Both metallic Ni- and Fe- based catalysts as well as Ni-Fe bimetallic catalysts have been used in biomass gasification processes for tar elimination²⁶⁻²⁸. Ramli et al.²⁶ studied the production of hydrogen from steam gasification of palm kernel shell (PKS). In their work, zeolite β (BEA) supported bimetallic Fe and Ni catalysts have been prepared using a sequential impregnation method and calcined at temperatures between 500 and 700 °C. It is reported that a strong interaction between Ni and Fe was observed at higher calcination temperatures (700 °C) resulting in the stabilization of Fe³⁺ and Ni²⁺ ions in the lattice, and thus a higher yield of hydrogen was produced due to the promoting of the water-gas shift reaction. Ni-Fe/ α -Al₂O₃ bimetallic catalysts prepared by co-impregnation method have been investigated for the reforming of tar from the pyrolysis of cedar wood using a laboratory-scale continuous feeding dual-bed reactor at 550°C²⁸. The Ni loading amount was 12wt.%, and Fe was added with a Fe/Ni molar ratio between 0.13 and 2. It was reported that the surface of Fe atoms supplied oxygen species and the addition of Fe to Ni/ α -Al₂O₃ enhanced the catalytic performance regarding the production of gas and the suppression of coke deposition on the surface of the catalyst. However, excess addition of Fe decreased the catalytic activity by decreasing the amount of surface Ni atoms²⁸.

There are few reports using Ni-Fe bimetallic catalyst for gasification of real biomass. In this work, co-precipitated NiO-Fe₂O₃-Al₂O₃ catalysts were prepared and investigated for hydrogen production from catalytic steam reforming of vapours derived from the pyrolysis of wood sawdust. It is aimed to develop an efficient catalyst for hydrogen production from biomass gasification in relation to the yield of hydrogen and the stability of catalyst (e.g. less coke formation on the surface of the catalyst and the prohibition of metal sintering). In particular, various molar ratios between Fe and Ni (1:9, 2:8, 4:6, 5:5, 6:4, 8:2 and 9:1) were studied, while the molar content of Al (support) was kept constant at 80%.

2. Experimental

2.1. Materials

Wood sawdust was used as raw biomass material, which has been reported in our previous report²⁹. Proximate analysis of the biomass sample showed that the sample contains about 6.4 wt.% moisture, 74.8 wt.% volatiles, 18.3 wt.% fixed carbon and 1.2 wt.% ash. Additionally, an element analysis showed that the biomass sample has 5.9 wt.% of hydrogen, 47.1 wt.% of carbon, 0.1 wt.% of nitrogen and 46.9 wt.% of oxygen (obtained from mass difference).

NiO-Fe₂O₃-Al₂O₃ catalysts with various Ni:Fe molar ratios (9:1, 8:2, 6:4, 5:5, 4:6, 2:8 and 1:9) were synthesized using a co-precipitation method, when the molar amount of Al molar was kept constant at 80%. It is noted that the molar ratio of Ni and Fe in the catalyst was fixed at 20%. During the preparation of catalyst, certain amounts of Ni(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, Al(NO₃)₃·9H₂O were dissolved in deionized water. NH₃·H₂O solution (2 mol L⁻¹) was slowly added to the above mixture to reach a pH value of 8. The suspension was kept at 60 °C within a water bath for one hour with continuously stirring. Filtration of the suspension was carried out afterward and the filtration cake was repeatedly washed with deionized water until a pH value of 7 was reached. The derived catalyst precursor was dried in an oven at 80°C for about 10 h, followed by calcination at 800 °C for 4 h within static air (heating rate was 1 °C min⁻¹). Finally, the catalyst was ground to small particles with a size between 50 and 180 μm, and assigned as fresh catalyst.

2.2. Reaction system for catalytic steam biomass gasification

A two-stage fixed bed reaction system was used to test the developed catalysts for hydrogen production. The reaction system has been reported in our previous work²⁹. In general, the biomass sample (wood sawdust) was pyrolyzed in a first reactor, and the derived vapours excluding the bio-char (retained in the first reactor) passed through a second reactor where catalyst and steam were presented to produce hydrogen-enriched syngas.

For each experiment, 0.25 g fresh catalyst (non-reduced) and 0.8 g biomass sample were used. Steam was generated by injecting water into the second reactor using a syringe pump. The water injection rate was 4.74 g h⁻¹. Carrier gas (N₂) with a flow rate of 80 ml min⁻¹ was introduced into the reaction system before heating the reactors. The second reactor was initially heated to 800 °C, then the first reactor was heating to 535°C with a heating rate of 40 °C min⁻¹. The products derived from the second reactor were introduced into a condensation system including an air cooled condenser and a dry-ice cooled condenser. The non-condensable gases were collected using a 25L TedlarTM gas bag.

The products (solid char residue and gas) and also the mass balance were obtained using the following equations. It is noted that the collected liquid contained both oil product and unreacted water. In addition, hydrogen-enriched gas was the main product. Thus oil production was not evaluated in this work.

$$\text{Gas yield (wt. \%)} = \frac{\text{Weight of gas}}{\text{Weight of biomass sample + water of injected water}} \times 100 \quad \text{Equation (1)}$$

$$\text{Char residue yield (wt. \%)} = \frac{\text{Weight of char residue}}{\text{Weight of biomass sample + water of injected water}} \times 100 \quad \text{Equation (2)}$$

$$\text{Mass balance} = \frac{\text{Weight of char residue, gas and liquid}}{\text{Weight of biomass sample + water of injected water}} \times 100 \quad \text{Equation (3)}$$

2.3. Gas analysis and characterisations of catalysts

2.3.1. Gas analysis

Concentrations of the non-condensable gases mainly including C₁₋₄ hydrocarbons, CO, CO₂, H₂ and N₂ were analysed by gas chromatography (GC) (Varian 3380). A flame ionization detector (FID) and an 80-100 mesh HayeSep column were used to detect C₁ to C₄ hydrocarbon gases (N₂ as carrier gas). Thermal conductivity detector and a HayeSep 80-100 mesh column were used to determine the concentrations of CO, CO₂, H₂ and N₂. It is noted that calibrations were carried out to all the mentioned gases (argon as carrier gas).

2.3.2. Characterisations of catalysts

The surface area of the prepared catalyst was analysed in this work. During the analysis, nitrogen gas was used as the adsorbate, and the specific surface area of the fresh catalyst was determined by N₂ adsorption isotherms on a Quantachrome Autosorb-1 Instrument. Before the isotherm analysis, about 150 mg of catalyst was loaded and degassed under vacuum at 150 °C for 5 hours, and the surface area was then measured under liquid nitrogen. Five points within a P/P₀ range from 0.05 to 0.25 were collected, and the specific surface area was calculated using the five-point BET method.

Temperature programmed reduction of the prepared catalysts was carried out using a modified thermogravimetric analyzer (SDT Q600). Fresh catalyst was loaded in an alumina pan and placed in the thermogravimetric analyzer furnace. The furnace reaction area was purged by a flow containing 15% H₂ and 85% N₂ with a 100mL min⁻¹. The catalysts were heated from room temperature to 1200°C at a rate of 10°C min⁻¹.

Temperature-programmed oxidation (TPO) of reacted catalysts was carried out using a Stanton-Redcroft thermogravimetric analyzer to determine the properties and the weight of the coked carbons deposited on the surface of reacted catalysts. About 25 mg of reacted catalyst was heated in an atmosphere of air with a heating rate of $15^{\circ}\text{C min}^{-1}$ to a final temperature of 800°C .

Catalysts were also analysed using scanning electron microscopy (SEM) (LEO 1530) and transmission electron microscopy (TEM) (Philips CM120 BioFilter) to obtain detailed morphologies of fresh and reacted catalysts. In addition, X-ray diffraction (XRD) was also carried out to the fresh catalysts. During the XRD analysis, a SIEMENS D5000 equipment was used in a range of $10\text{-}70^{\circ}$ with a scanning step of 0.02° using Cu $K\alpha$ radiation. The shape factor K is 0.89, X-ray wavelength of the Cu radiation is 0.1542 nm, B was obtained from Jade 5.0 (XRD analysis software) as FWHM values. Crystalline phase identification was carried out by comparison with the Joint Committee on Powder Diffraction Standards (JCPDS) standards.

3. Results and discussion

3.1. Characterizations of fresh NiO-Fe₂O₃-Al₂O₃ catalysts

3.1.1 N₂ adsorption analysis

Textural properties, theoretical metal composition, crystal size obtained from XRD analysis and BET surface area are shown in Table 1. The fresh co-precipitated NiO-Fe₂O₃-Al₂O₃ catalysts show relatively high BET surface areas ranging from 110.3 to $170.7\text{ m}^2\text{ g}^{-1}$. The specific BET surface area increased from 110.3 to $170.7\text{ m}^2\text{ g}^{-1}$, then slightly decreased to $152.1\text{ m}^2\text{ g}^{-1}$ when the Ni:Fe molar ratio was increased from 1:9 to 9:1. The surface area has been reported to be enhanced with the increase of Ni content by Yu et al.³⁰, who suggested that the increased fraction of spinel phase might contribute to the increase of BET surface area.

3.1.2. XRD analysis

XRD patterns of the fresh NiO-Fe₂O₃-Al₂O₃ catalysts are shown in Fig. 1 using the Joint Committee on Powder Diffraction Standards (JCPDS) file as a reference. The identifiable phases of the XRD patterns include NiAl₂O₄ (JCPDS 78-0552) and γ -Al₂O₃ (29-0063) for all the fresh NiO-Fe₂O₃-Al₂O₃ catalysts. The diffraction peaks at 2θ of 31.4° , 37.0° , 45.0° , 59.6° and 65.5° for stoichiometric NiAl₂O₄ spinel phase were clearly displayed as shown in Fig. 1. Chen et al.³¹ reported that when Al³⁺ was rich in Ni-Al catalyst, Ni²⁺ coordinated with Al³⁺

dominantly to form NiAl_2O_4 spinel phase. It is noted that Wang et al.³² and López-Fonseca et al.³³ reported that diffraction lines for NiAl_2O_4 (JCPDS 78-0552) at 2θ positions (37.0° , 45.0° , 65.5°) overlap diffraction peaks of $\gamma\text{-Al}_2\text{O}_3$ at similar 2θ positions (37.6° , 45.8° , 66.8°), which was also observed in Fig. 1.

However, for the fresh $\text{NiO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalysts with Ni:Fe molar ratios of 9:1, 8:2, 6:4, 5:5 and 4:6, there were no clear evidence to prove the appearance of Fe species, which may result from the fact that the particle size of Fe species was too small to be detected³⁴. In addition, it is also difficult to identify NiO particles; this might be also due to the presence of small NiO particles. By further increasing Fe content (the $\text{NiO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalyst with Ni:Fe molar ratio of 1:9), the diffraction lines of $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS 33-0664) at 2θ positions of 24.1° , 33.1° , 35.6° , 40.8° , 43.5° , 49.4° , 54.0° , 57.5° and $\gamma\text{-Fe}_2\text{O}_3$ (JCPDS 39-1346, $2\theta=23.8^\circ$, 26.1° , 32.1° , 33.9° , 35.6° , 37.2° , 40.4° , 43.3° , 50.0° , 53.7° , 54.9° , 57.3°) were identified; this might be due to the increased content of Fe in the catalyst. The particle size for NiAl_2O_4 spinel calculated at the 2θ position of 45.0° and the particle size for $\gamma\text{-Al}_2\text{O}_3$ calculated at 65.5° in $\text{NiO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalyst were both about 5 nm.

3.1.3. SEM analysis

The SEM images of fresh $\text{NiO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalysts with scale bar of 1 μm are shown in Fig. 2. With the change of Ni:Fe molar ratios, the morphology of catalysts only changed slightly with similar morphologies. The micrographs which can be seen from Fig. 2 show the presence of agglomerates composed of small quasi-spherical particles for all fresh $\text{NiO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalysts. However, due to the fact that the particle size of crystal phases in fresh $\text{NiO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalysts is only around 5nm (Obtained from XRD analysis and shown in Table 1), the particles of crystal phases are difficult to be observed using SEM analysis.

3.1.4. TEM analysis

The TEM images of the selected catalysts including the fresh 9Ni1FeAl, 5Ni5FeAl and 1Ni9FeAl catalysts are depicted in Fig. 3. A high dispersion of metal particles can be observed, with a homogeneous distribution in a form of small well-dispersed particles. The particle size obtained from TEM images is around 5nm which is in agreement with the XRD results (shown in Table 1) for both the fresh 9Ni1FeAl and 5Ni5FeAl catalysts. With the increase of Fe:Ni molar ratio to 9:1, the size of metal particles was increased significantly as shown in Fig. 3 (c).

However, it was impossible to distinguish NiAl_2O_4 , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ from the TEM analysis (Obtained from XRD results shown in Fig. 1).

3.1.5. TPR analysis

TPR analysis of fresh catalysts are shown in Fig. 4 to obtain the thermal stabilities of catalysts, and the interaction between metal and support. There is a wide H_2 consumption temperature window from 300 to 1050 °C with a maximum value at around 800 °C and two other smaller reduction peaks at approximate 420 and 550 °C, respectively, for all the fresh catalysts.

For the fresh $\text{NiO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3$ catalysts with a Ni:Fe molar ratio of 9:1, there is another extra small reduction peak at about 250 °C which might be attributed to the transformation from Fe_2O_3 to Fe_3O_4 , which was also reported by other researchers³⁵.

Chen et al.³¹ reported that the reduction peak at around 800 °C might be assigned as the reduction of stoichiometric NiAl_2O_4 spinel phase, which was also identified by the XRD results (Fig. 1) and other researchers^{36,37}. In addition, according to Ayub et al.³⁸ and Ratkovic et al.³⁹, the reduction peaks at around 420, 550 and 800 °C can be assigned as the reduction of $\gamma\text{-Fe}_2\text{O}_3$. The reduction of Fe-oxide species in the literature is usually reported as two- or three-step process ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$ or $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$) depending on the weight of the sample, composition of reducing agent and the particle size of metal oxides⁴⁰.

With the decrease of Ni content and the increase of Fe content, for example, when the Ni:Fe molar ratio was decreased to 5:5, 4:6, 2:8 and 1:9, two small reduction peaks at around 420 and 550 °C were clearly observed. The maximum reduction temperature was slightly increased to 830 °C and the width of the peak was enhanced with the increase of Fe content, indicating more metal oxide species were reduced and the reducibility was reduced for the bimetallic catalysts³⁹.

3.2. Catalytic steam gasification of biomass

3.2.1. Mass balance

The yields of gas, solid residue and mass balance are presented in Table 2. The residue yield was around 36.3 wt.% for each experiment, since pyrolysis at the first stage was the same. It is noted that the amount of carbon formed inside the second reactor was negligible by weighting the reactor before and after the experiment. As mentioned previously, the liquid collected in the condensation system contains both unreacted water and oil, as the oil was not the key target

of this work, detailed oil analysis was not carried out. The mass balance showed that reliable results were obtained from the experiments to support discussions.

When the steam reforming of the derived vapours from pyrolysis of wood sawdust was carried out with a sand bed (as a 'blank' comparative material within the second reactor), the gas yield related to the mass of wood sawdust was 33.0 wt.%, and the hydrogen production was 2.4 mmol ($\text{H}_2 \text{ g}^{-1}$ wood sawdust). The production of hydrogen is calculated by the molar of hydrogen divided by the weight of the biomass sample used in each experiment. When the reforming process was performed with the addition of NiO-Fe₂O₃-Al₂O₃ catalysts, both the gas and hydrogen yields were enhanced significantly. For example, the gas yield was increased from 33.0 to 62.8 wt.% and the hydrogen production was increased from 2.4 to 11.4 (mmol $\text{H}_2 \text{ g}^{-1}$ wood sawdust). The highest gas and hydrogen yields were obtained with the 9Ni1FeAl catalyst, indicating that Ni played an important role for hydrogen and gas production in the process of catalytic steam thermo-chemical conversion of biomass.

The relationship between Ni content and catalytic reactivity have been investigated by other researchers. Barroso et al.⁴¹ studied hydrogen production from steam reforming of ethanol using NiZnAl catalysts with different Ni loadings; it was reported that with the increase of Ni content, both the gas and hydrogen yields were increased. In our previous work, Ni/MCM41 catalysts with different Ni loadings ranging from 5 to 40 wt.% were used for catalytic thermo-chemical conversion of wood sawdust, also both the gas and hydrogen yields were increased with the increase of Ni loadings. It is therefore suggested that a well distributed and increased metal particle content (e.g. Ni) is one of the key factors to enhance hydrogen production from catalytic thermo-chemical conversion of hydrocarbons⁴².

With the decrease of Ni content or increasing the Fe content, both gas and hydrogen yields were decreased and then increased, indicating that Fe content also influenced gas and hydrogen yields. According to Nordgreen et al.²¹, metallic iron obtained by reducing iron oxides (FeO, Fe₂O₄ and Fe₃O₄) significantly reduced the content of tar, a mixture of hydrocarbons produced from biomass gasification. Kuhn et al.⁴³ investigated catalytic steam reforming of tar in the presence of olivine catalysts; they reported that Fe-related species increased significantly the production of hydrogen, compared to the experiment using only olivine. Similar contributions of Fe-related species to hydrogen production was also reported by Devi et al.⁴⁴, when catalytic steam reforming of naphthalene (a model biomass tar compound) was carried out.

As shown in Table 2, when the molar ratio of Ni:Fe was higher than 1, the gas and hydrogen yields were higher than the catalysts with the Ni: Fe molar ratio less than 1, indicating that Ni played a dominant role for hydrogen production compared to Fe, which is consistent with other literature ⁴⁵. It is suggested that Ni-species have high catalytic ability to break down C-H and C-C bonds compared to Fe-species.

With decreasing the Ni:Fe molar ratio from 9:1 to 2:8, both gas and H₂ yields were decreased. By further decreasing the Ni:Fe molar ratio, the gas and H₂ yields were increased slightly, but were still lower compared to the catalysts with the Ni:Fe molar ratio larger than 1. This might be ascribed to the presence of Fe oxides as shown in the XRD analysis (Fig. 1). Similar results have been reported by Wang et al. ²⁸, in the steam reforming process of tar carried out with Ni-Fe/ α -Al₂O₃ catalysts, the addition of Fe to Ni/ α -Al₂O₃ promoted the steam reforming reaction monotonously in the range of the molar ratio of Fe to Ni (Fe/Ni) \leq 0.5, and the amount of tar decreased. In contrast, the excess addition of Fe (Fe/Ni > 0.5) decreased the formation rate of gaseous products. High activity of Ni-Fe/ α -Al₂O₃ catalysts can be caused by the synergy between Ni and Fe. It has been reported that Ni-Fe bimetallic catalysts derived from LaNi_{0.3}Fe_{0.7}O₃ were effective for the gasification of almond shell and steam reforming of methane ⁴⁶.

3.2.2. Gas concentration

As shown in Table 2, when the pyrolysis and steam gasification process was carried out with a sand bed, the H₂ content was 17.4vol.%, CO content was 45.5vol.%, CO₂ content was 14.5vol.%, CH₄ content was 14.8vol.% while C₂-C₄ content was 7.8vol.%.

Compared with non-catalytic steam gasification of wood sawdust, the H₂ concentration was increased to 37.2vol.%, CO₂ concentration was enhanced to 21.3vol.% while CO, CH₄ and C₂-C₄ concentration were all decreased, to 27.4, 6.2 and 1.2vol.%, respectively, during the steam gasification process in the presence of NiO-Fe₂O₃-Al₂O₃ catalysts. This suggests that the water-gas shift reaction (Equation 5), reforming and decomposition of hydrocarbons and oxygenated compounds (Equation 4 to Equation 9) were possibly promoted with Ni-based catalysts, Fe-based catalysts and/or bimetallic Ni-Fe based catalysts ^{21, 28, 47, 48}.

With the increase of Fe content, the CO composition in the catalytic performance of steam gasification process was firstly decreased from 41.6 to 27.4vol.%, then increased to 30.3vol.%. H₂ composition ranged from 37.2 to 32.7vol.%, CO₂ composition was increased from 14.5 to

21.3vol.%, both CH₄ and C₂-C₄ compositions were firstly increased then decreased, from 6.2 to 13.7vol.%, then to 12.1vol.% and from 1.2 to 4.1vol.%, then to 3.4vol.%, respectively.



The decrease of CO fraction indicated that the water-gas shift reaction (Equation 5) was enhanced by the addition of catalysts. The lowest CO content was generated with the 5Ni5FeAl catalyst, indicating the water-gas shift reaction (Equation 5) was promoted to the largest extent in the presence of the 5Ni5FeAl catalyst. In addition, when the Ni:Fe molar ratio was larger than 1, the contents of CO₂, CH₄ and C₂-C₄ content were smaller than that produced with Ni:Fe ratio smaller than 1, indicating there was an optimal addition of Fe-species for the promotion of water-gas shift reaction (Equation 5) and hydrocarbon decomposition reaction (Equation 6). However, the H₂ composition was higher when the Ni:Fe molar ratio was larger than 1. Thus it is suggested that hydrogen production was mainly contributed by Ni-species in the NiO-Fe₂O₃-Al₂O₃ catalyst.

According to gas composition data in Table 2 and Fig. 5, although the highest gas and H₂ yields were obtained with the 9Ni1FeAl catalyst, the highest H₂/CO ratio, and lowest CO/CO₂ ratio were obtained with the utilization of the 5Ni5FeAl catalyst. The H₂/CO molar ratio showed a trend of an initial increase from 0.4 to 1.3, and then decreased to 1.1, when the Ni:Fe ratio was reduced from 9:1 to 1:9; while the CO/CO₂ molar ratio has an opposite trend, which was firstly decreased from 3.1 to 1.3, then increased to 1.5. It is demonstrated that the increase of Fe content promoted the water-gas shift reaction (Equation 5) and this reaction was promoted to the largest extent when the 5Ni5FeAl catalyst was present in the steam gasification process.

Polychronopoulou et al.⁴⁹ investigated an adsorption-enhanced steam reforming process of phenol (a model compound of wood biomass pyrolysis oil) carried out with supported Fe catalysts, the optimum loading of Fe for maximum H₂ yield was 5 wt.%. According to Orío et al.⁴², four different dolomites with varying Fe₂O₃ content were investigated for oxygen/steam

gasification of wood, the dolomite with highest Fe₂O₃ content exhibited the highest activity with 95% tar conversion.

Based on the research work of Wang et al.³², the catalytic performance of NiO-Fe₂O₃-Al₂O₃ catalyst for partial oxidation showed that the conversion of methane and the selectivity of CO and H₂ were 90.09, 97.28 and 97.09%, respectively at 875°C. According to Wang et al.⁵⁰, the utilization of co-precipitated Ni-Fe catalysts for hydrogen production from partial oxidation of ethanol (a model compound of biomass derived by-product) was performed, the Ni₅₀Fe₅₀ catalyst showed the best activity in terms of the ethanol conversion and the selectivity of hydrogen.

3.2.3. Coke deposition on used catalysts

The used catalysts were characterized by TPO analysis and the results are shown in Fig. 6 via weight change intensity (mg) versus temperature (°C). Two oxidation stages in the TPO analysis are observed, the first oxidation peak is ascribed to the oxidation of metal particles and the second peak was for carbon oxidation. The peaks of increasing mass from 300 to 600°C and above 700°C were associated with the oxidation of Ni and Fe species during the TPO analysis. The reduced metal species were suggested to be produced during the pyrolysis and steam reforming process where reduction agent H₂ and CO were present²⁹. Therefore, the reduction of fresh catalysts before the reaction is unnecessary, which reduced the operation cost.

Weight loss before 550°C for the TPO analysis is suggested to be assigned to the oxidation of amorphous carbon. The oxidation peak at a higher temperature which starts from 550 to 700°C might be attributed to the oxidation of filamentous carbon deposited on the surface of the reacted catalyst⁵¹. The amount of coke formation was calculated as the weight loss except for the oxidation of metal divided by the initial sample weight during the TPO experiment. It is proposed that the total amount of coke deposition on the used catalyst was less than 2wt.% in relation to the weight of the used catalyst with a Ni:Fe molar ratio of 1:9, indicating that a high stability of catalyst resistant to coke deposition. At the temperature of 800°C, carbon gasification reaction and Boudouard reaction (Equation 8 and Equation 9) contribute to the reduction of coke formation as suggested by Sutton et al.⁴². Corujo et al.⁵² reported a more than 5 wt.% amount of coke formation on a Ni/dolomite catalyst for steam gasification of forestry residue and an even higher amount (>10wt.%) of coke formation was obtained on a reacted Ni/Al₂O₃ catalyst for the steam gasification of biomass reported by Nishikawa et al.⁵³.

SEM analysis, shown in Fig. 7, confirms the presence of amorphous and filamentous carbon on the surface of the used catalysts with a Ni:Fe ratio larger than 1 and there was almost no carbon deposition on the surface for the reacted catalysts with a Ni:Fe ratio smaller than 1. Wang et al.²⁸ reported that one of the drawbacks of using Ni-based catalysts during steam reforming of biomass tar was carbon deposition on the surface of metallic Ni species, while Ni-Fe alloy species could resist the formation of coke. Therefore, they reported the addition of Fe suppressed the carbon deposition on the surface of the reacted catalyst.

Although the filamentous carbon was confirmed by the SEM images, due to the low amount of coke deposited on the used catalyst, it was not identified from the TEM analysis as shown in Fig. 8. TEM analysis of the size of metal particle (~4 nm) inside the reacted 9Ni1FeAl (Fig. 8) was similar to the results shown in Fig. 3 (fresh catalyst), indicating sintering was not serious after the catalytic reforming of vapour produced from pyrolysis of sawdust.

Conclusions

In this work, NiO-Fe₂O₃-Al₂O₃ catalysts with different Ni:Fe molar ratios (9:1, 8:2, 6:4, 5:5, 4:6, 2:8 and 1:9) prepared by co-precipitation method have been investigated for hydrogen-rich syngas production from pyrolysis and steam reforming of wood sawdust. The prepared catalyst has well-dispersed NiAl₂O₄, α -Fe₂O₃ and γ -Fe₂O₃ crystal phases. The high dispersion of metal species was proved to enhance the catalyst stability in terms of coke formation on the surface of the used catalyst and the sintering of metal particles. Both gas and hydrogen yields were increased significantly when catalysts were added into the gasification process, gas production was increased from 33.0 to 62.8 wt.% and the H₂ yield was enhanced from 2.4 to 11.4 mmol g⁻¹ wood sawdust with the 9Ni1FeAl catalyst. The enhanced hydrogen production was suggested to be due to the increased number of catalytic sites during the biomass gasification process and both Ni and Fe metal (mainly Ni) promoted the steam gasification process. Coke deposition on the reacted 1Ni9FeAl catalyst (<2wt.%) was suggested to be negligible. The increase of Fe addition to the NiO-Fe₂O₃-Al₂O₃ significantly reduced the amount of coke formed on the surface of the catalyst, as obtained from the TPO analysis of the reacted catalyst.

Acknowledgement

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Table 1: Textural characteristics of fresh NiO-Fe₂O₃-Al₂O₃ catalysts.

Sample	Molar ratio (Ni:Fe)	Theoretical Metal Composition (wt.%) ^a			Particle size(nm) ^b		BET surface area (m ² /g)
		Ni	Fe	Al ₂ O ₃	NiAl ₂ O ₄	Y-Al ₂ O ₃	
1Ni9FeAl	1:9	2.3	19.3	78.4	-	-	110.3
2Ni8FeAl	2:8	4.5	17.2	78.3	5.0	3.5	123.5
4Ni6FeAl	4:6	9.0	12.8	78.2	4.2	3.4	141.2
5Ni5FeAl	5:5	11.2	10.7	78.1	4.4	3.6	146.5
6Ni4FeAl	6:4	13.5	8.5	78.0	4.5	5.3	141.8
8Ni2FeAl	8:2	17.9	4.3	77.8	4.7	4.4	170.7
9Ni1FeAl	9:1	20.1	2.2	77.7	4.5	4.4	152.1

^aThe theoretical metal composition was calculated via the equation $M=M/(Ni+Fe+Al_2O_3)$, where M represents Ni or Fe (wt.%).

^bThe particle size was calculated based on XRD result shown in Figure 5-1.

Table 2: Mass balance and gas compositions from pyrolysis and steam gasification of wood sawdust.

Catalyst bed	Sand	9Ni1FeAl	8Ni2FeAl	6Ni4FeAl	5Ni5FeAl	4Ni6FeAl	2Ni8FeAl	1Ni9FeAl
Gas/Wood sawdust (wt.%)	33.0	62.8	57.1	58.4	51.3	49.6	50.0	53.2
Residue/Wood (wt.%)	38.8	37.5	36.3	36.3	36.3	37.5	36.3	36.3
Mass balance (wt.%)	103.3	100.6	102.4	88.5	99.2	99.4	97.6	101.8
H ₂ yield (mmol H ₂ g ⁻¹ wood)	2.4	11.4	10.7	9.2	8.7	8.4	7.7	8.3
Gas composition (vol.%, N ₂ free)								
CO	45.5	41.6	32.9	38.0	27.4	28.0	30.3	29.8
H ₂	17.4	36.5	37.2	33.6	35.2	34.8	32.7	33.4
CO ₂	14.5	14.5	17.6	18.3	20.9	20.4	19.9	21.3
CH ₄	14.8	6.2	10.3	8.0	13.4	13.7	12.9	12.1
C ₂ -C ₄	7.8	1.2	2.1	2.1	3.1	3.1	4.1	3.4

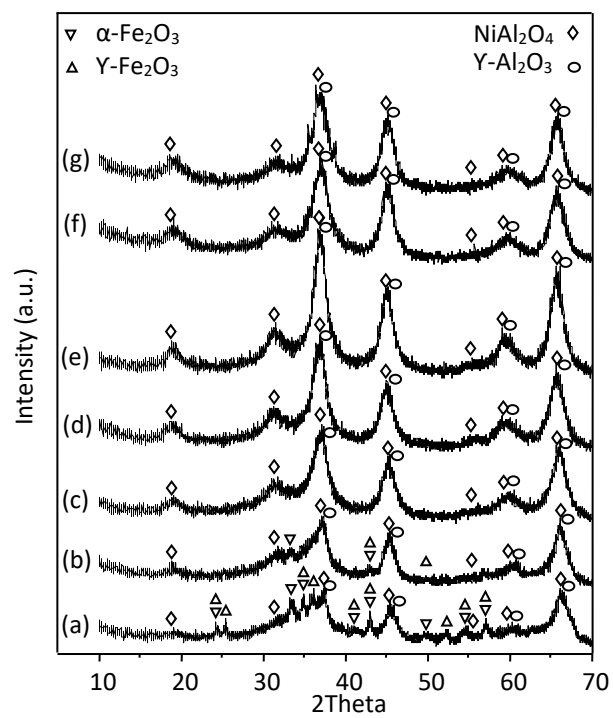
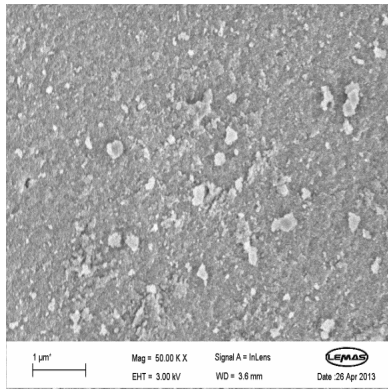
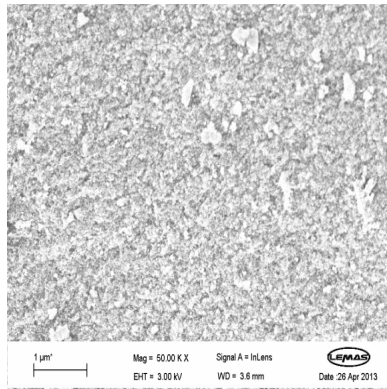


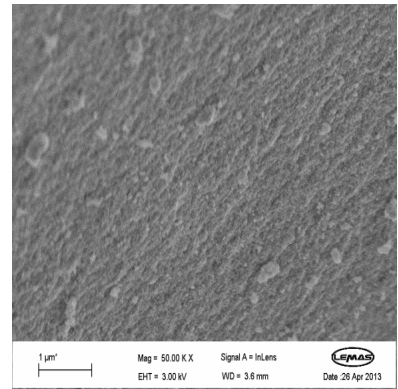
Fig. 1: XRD results for fresh NiO-Fe₂O₃-Al₂O₃ catalysts with different Ni:Fe ratios; (a): 1:9; (b): 2:8; (c): 4:6; (d): 5:5; (e): 6:4; (f): 8:2; (g): 9:1.



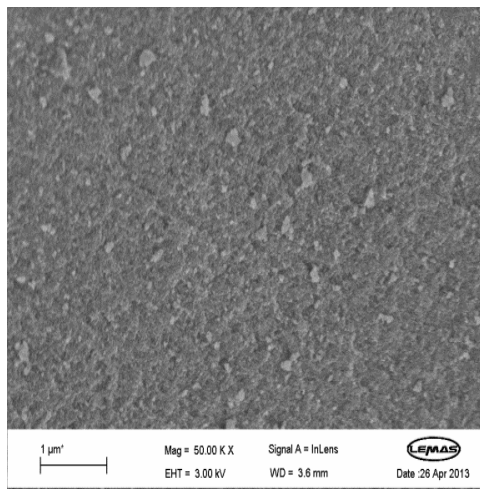
(a): Ni:Fe = 9:1;



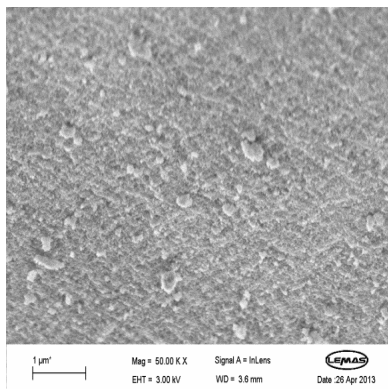
(b): Ni:Fe = 8:2;



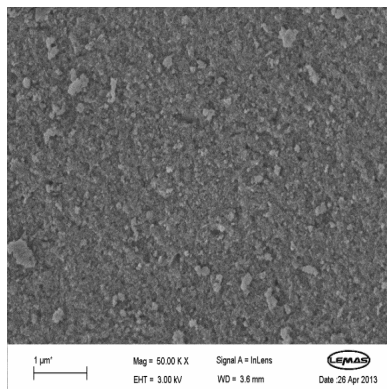
(c): Ni:Fe = 6:4;



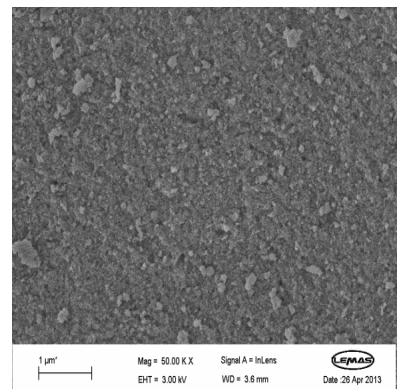
(d): Ni:Fe = 5:5;



(e): Ni:Fe = 4:6;

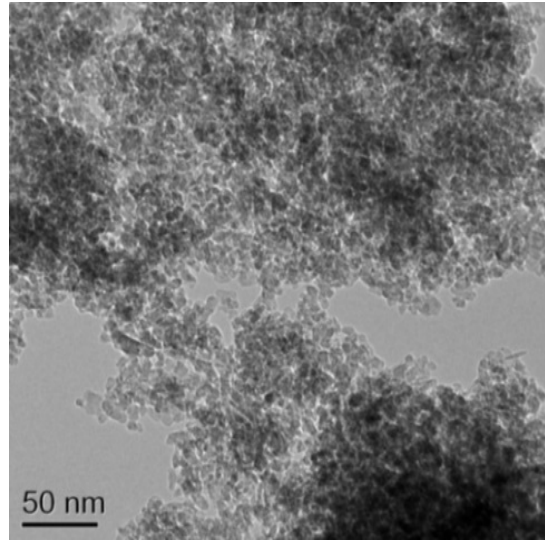
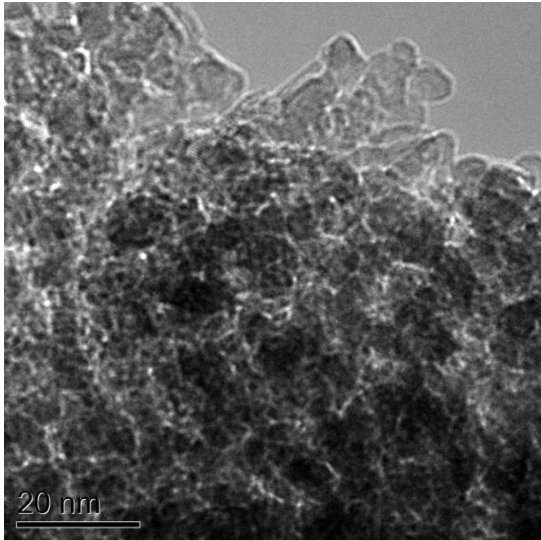


(f): Ni:Fe = 2:8;

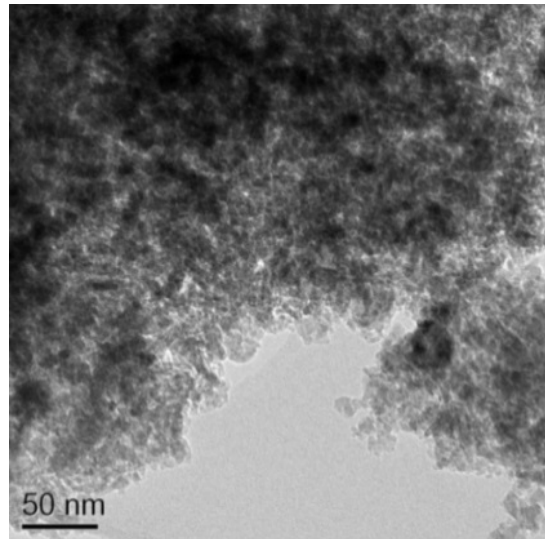
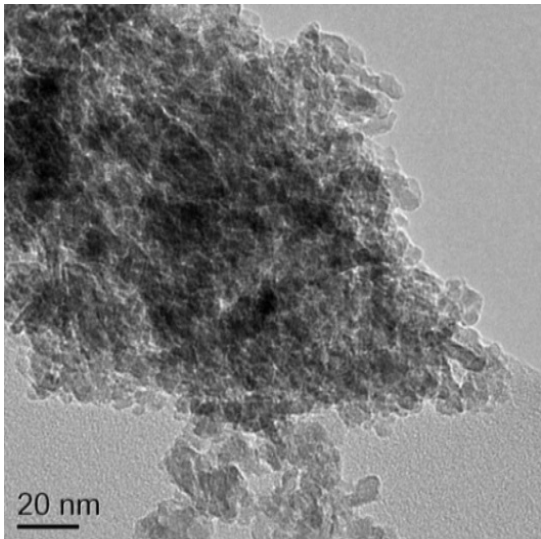


(g): Ni:Fe = 1:9.

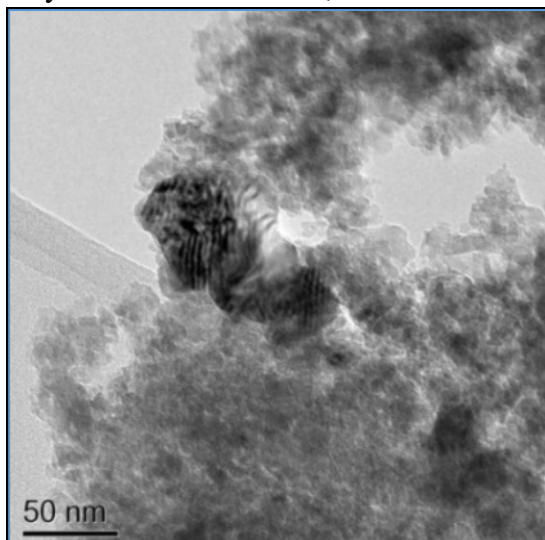
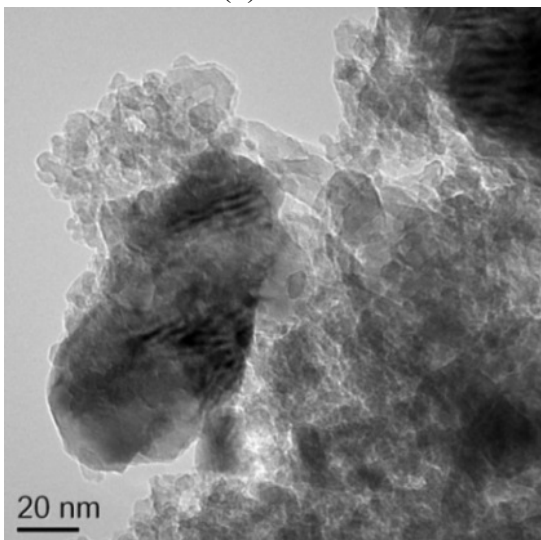
Fig. 2: SEM results of fresh NiO-Fe₂O₃-Al₂O₃ catalysts with various Ni:Fe ratios.



(a): fresh NiO-Fe₂O₃-Al₂O₃ catalyst with a Ni:Fe = 9:1;



(b): fresh NiO-Fe₂O₃-Al₂O₃ catalyst with a Ni:Fe = 5:5;



(c): fresh NiO-Fe₂O₃-Al₂O₃ catalyst with a Ni:Fe = 1:9.

Fig. 3: TEM analysis results of fresh NiO-Fe₂O₃-Al₂O₃ catalysts with various Ni:Fe molar ratios.

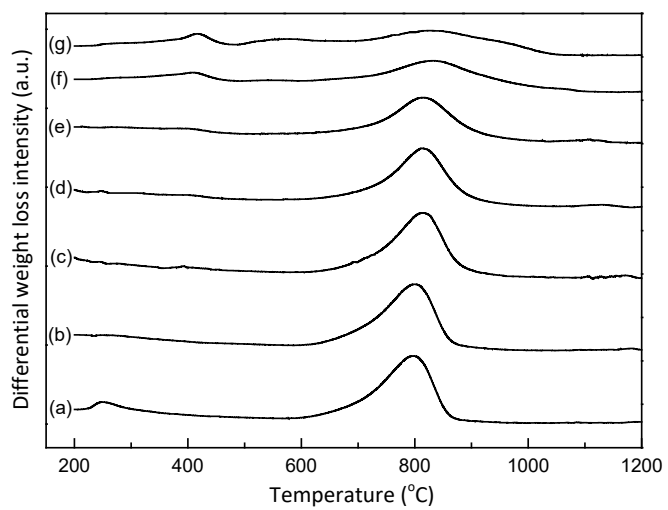


Fig. 4: Differentiated weight loss intensity results of fresh NiO-Fe₂O₃-Al₂O₃ catalysts with different Ni:Fe ratios; (a): 9:1; (b): 8:2; (c): 6:4; (d): 5:5; (e): 4:6; (f): 2:8; (g): 1:9.

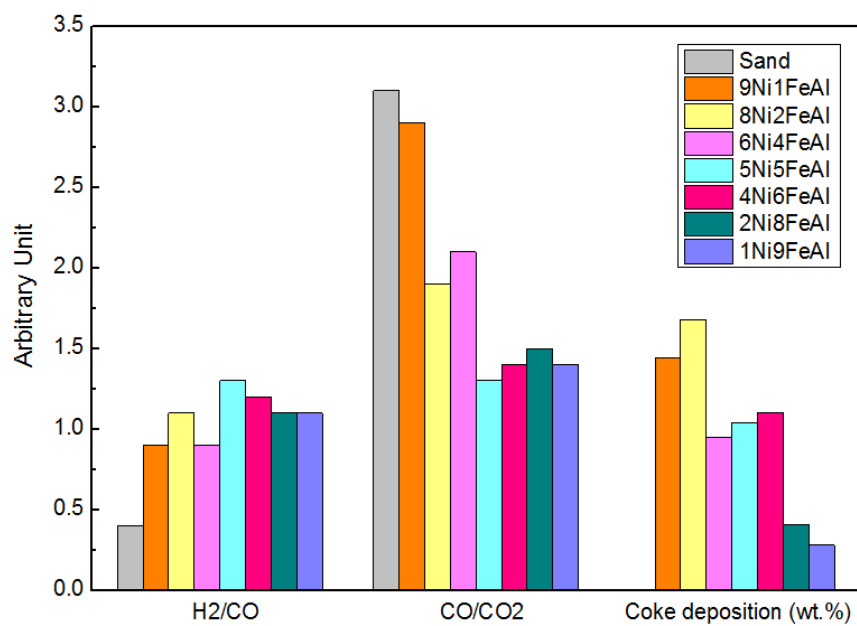


Fig. 5: H₂/CO, CO/CO₂ molar ratios based on gas composition in Table 2 and coke deposition based on TPO results in Fig.6.

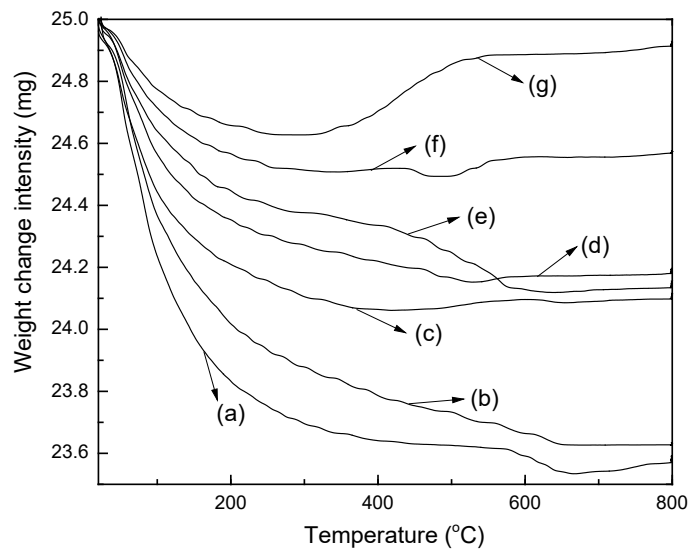
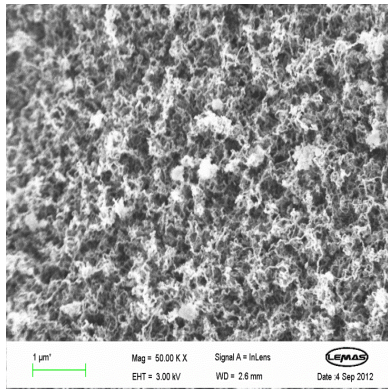
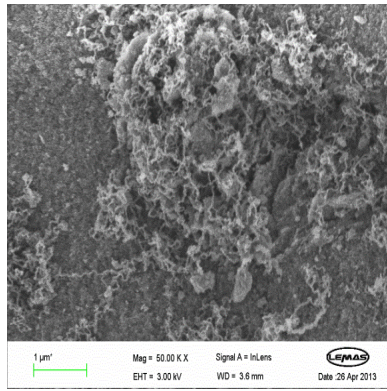


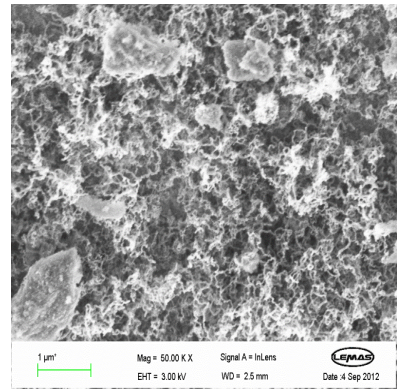
Fig. 6: Weight change intensity of used NiO-Fe₂O₃-Al₂O₃ catalysts with different Ni:Fe ratios; (a): 9:1; (b): 8:2; (c): 6:4; (d): 5:5; (e): 4:6; (f): 2:8; (g): 1:9.



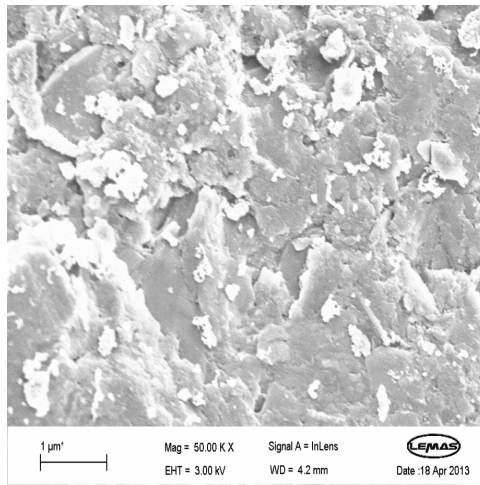
(a): used, Ni:Fe = 9:1;



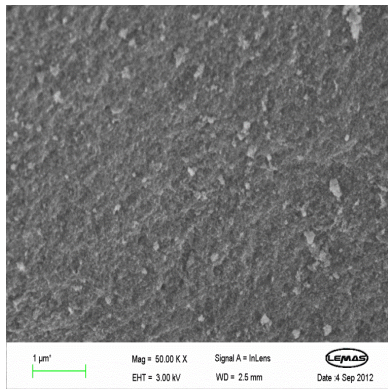
(b): used, Ni:Fe = 8:2;



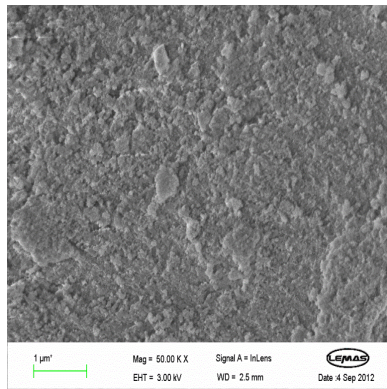
(c): used, Ni:Fe = 6:4;



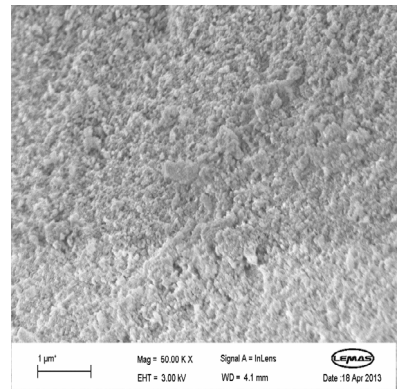
(d): used, Ni:Fe = 5:5;



(e): used, Ni:Fe = 4:6;



(f): used, Ni:Fe = 2:8;



(g): used, Ni:Fe = 1:9.

Fig. 7: SEM results of used NiO-Fe₂O₃-Al₂O₃ catalysts with various Ni:Fe ratios.

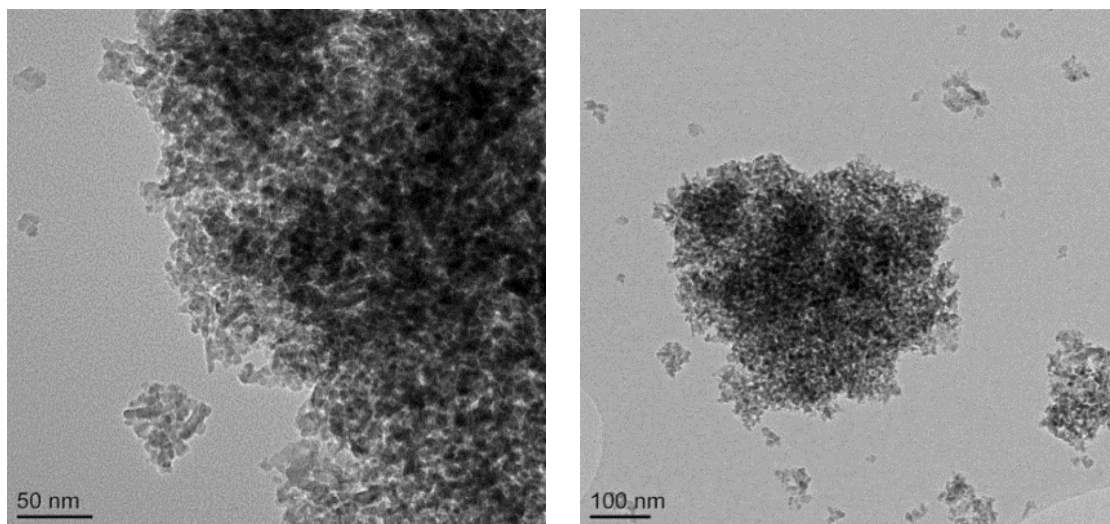


Fig. 8: TEM results of used NiO-Fe₂O₃-Al₂O₃ catalysts with a Ni:Fe molar ratio of 9:1.