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Promoting Hydrogen Production and Minimizing Catalyst Deactivation from the Pyrolysis-Catalytic Steam Reforming of Biomass on nanosized NiZnAlO_x Catalysts

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Abstract: Hydrogen production from the thermochemical conversion of biomass was carried out with nano-sized NiZnAlO_x catalysts using a two-stage fixed bed reactor system. The gases derived from the pyrolysis of wood sawdust in the first stage were catalytically steam reformed in the second stage. The NiZnAlO_x catalysts were synthesized by a co-precipitation method with different Ni molar fractions (5, 10, 15, 25 and 35%) and a constant Zn:Al molar ratio of 1:4. The catalysts were characterized by a wide range of techniques, including N₂ adsorption, SEM, XRD, TEM and temperature-programmed oxidation (TPO) and reduction (TPR). Fine metal particles of size around 10-11 nm were obtained and the catalysts had high stability characteristics, which improved the dispersion of active centers during the reaction and promoted the performance of the catalysts. The yield of gas was increased from 49.3 to 74.8 wt.%, and the volumetric concentration of hydrogen was increased from 34.7 to 48.1 vol.%, when the amount of Ni loading was increased from 5 to 35%. Meanwhile, the CH₄ fraction decreased from 10.2 to 0.2 vol.% and the C₂-C₄ fraction was reduced from 2.4 vol.% to 0.0 vol.%. During the reaction, the crystal size of all catalysts was successfully maintained at around 10-11 nm with lowered catalyst coke formation, (particularly for the 35NiZn4Al catalyst where negligible coke was found) and additionally no obvious catalyst sintering was detected. The efficient production of hydrogen from the thermochemical conversion of renewable biomass indicates that it is a promising sustainable route to generate hydrogen from biomass using the NiZnAl metal oxide catalyst prepared in this work via a two-stage reaction system.

Key Words: Biomass; Catalyst; Hydrogen; Coke; Sintering

1. Introduction

There are key environmental challenges for the use of fossil fuels in relation to energy security, environmental impact and the release of greenhouse gases. Therefore, there is global interest in the development of renewable and clean fuels as alternatives to fossil fuels [1-4]. Hydrogen is known as an ideal clean energy carrier for the production of heat and power, since its combustion releases only water [4, 5]. The utilization of hydrogen for electricity generation via fuel cells and power plant has been recognized, with high efficiencies and zero net contribution of CO₂ to the atmosphere [6]. Efforts are developing towards cost-efficient processes to produce sufficient hydrogen from renewable resources e.g. wind, hydropower, and biomass for commercial utilization [7-10]. Among these resources, biomass is abundantly available including cheap and non-food feedstocks, such as energy crops, agricultural residues, organic wastes, by-products from bio-refineries, wastes produced by the food industry and the biodegradable fraction of municipal solid waste [11, 12]. From a technical point of view, sustainable hydrogen produced from biomass by thermochemical processes e.g. gasification and pyrolysis has already been developed [13, 14, 15].

Therefore, biomass gasification and pyrolysis-steam reforming for hydrogen production has drawn great interest, particularly using steam as the gasification agent and a suitable catalyst where the hydrogen yield can be significantly enhanced [16-20]. However, a challenge towards large scale commercialisation is tar formation in the product syngas and coke formation on the catalyst; the tar can block the pipework of downstream applications and the coke deposits on the surface of the reacted catalyst lead to deactivation [21]. A desirable catalyst should promote tar reduction in the syngas, have good thermal stability in terms of prohibition of metal sintering and promote a high yield of hydrogen production. [21-23] A number of catalysts have been proven to be active for hydrogen production and are stable towards deactivation in biomass gasification/reforming, which are mainly the platinum group metals (e.g. Ph, Rt, Pd, Ru) based catalysts [23-27]. However, the high cost of noble metal-based catalysts discourages the practical application of biomass gasification/ pyrolysis-reforming. Therefore, to develop a cheaper and alternative metal-based catalyst would be desirable [4].

During the last decade, nickel-catalysts have been extensively investigated for biomass gasification and pyrolysis-catalytic steam reforming. For enhanced catalytic performance and

thermal stability, various supports (such as, zeolites [4, 5, 7, 28, 29], dolomite [1, 22, 30, 31], olivine [21, 32], other metal and metal oxides such as La, Fe, CeO₂, SiO₂, ZrO₂, TiO₂, MgO, ZnO, Al₂O₃ [10, 33-39]) have been applied to change the interactions between support and metal particles which may thereby influence the catalytic properties. Particularly, alumina has been widely investigated as a catalyst support due to high activity and low cost in the reforming process [33-35, 40]. However, catalysts based on an alumina support suffer severely from coke deposition because of the strong acidity of the alumina support [41]. Under this circumstance, modifications of Ni-based Al₂O₃ supported catalysts should be investigated by the addition of basic metals or promoters which can help decrease the support acidity and also improve the prohibition of coke formation on the surface of the catalyst and also the catalyst thermal stability [21].

The application of basic metal oxides [42, 43] as supports or as promoters [44, 45] into Al₂O₃ have been researched to enhance the catalytic performance and minimize the coke deposition. For example, Yang et al. [46] investigated the effect of catalyst supports on ethanol steam reforming (ESR) using Ni-based catalysts and reported that Ni/ZnO exhibited the highest hydrogen selectivity followed by Ni/MgO and Ni/Y-Al₂O₃. Ethanol steam reforming using ZnO/Al₂O₃ was carried out by Chen et al. [47], and it was found that the introduction of ZnO is beneficial to the reduction of CO production, avoiding the initial loss of catalytic activity and thus enhancing the long-term catalyst stability. Monzón et al. [48] also reported that the introduction of ZnO in Ni/Al₂O₃ increased the H₂ selectivity with reduced coke deposition. Abello et al. [3, 49] studied ethanol steam reforming with a Ni/Zn–Al catalyst prepared by a sol-gel method and found that the catalyst had high selectivity to H₂ and CO₂. In the methanol steam reforming reported by Yang et al. [50], ZnO-Al₂O₃ exhibited high hydrogen yield with low CO concentration. Therefore, the addition of basic ZnO into Ni-based Al₂O₃ catalysts could be promising for the process of steam gasification of biomass.

Biomass gasification has been investigated with single [21] or two-stage reaction systems [1, 4, 5, 7, 51]. Under the single stage reaction system, the samples and catalysts were mixed and the pyrolysis and gasification processes were operated under the same conditions, resulting in difficulty in the separation of catalysts and biomass residues after reaction [21]. A two-stage pyrolysis-catalytic steam reforming system can overcome this challenge and improve gas quality since the thermal degradation of the biomass and reforming of derived products are under different process conditions e.g. temperature.

In this work, co-precipitated NiO-ZnO-Al₂O₃ catalysts were prepared and used for the pyrolysis and subsequent catalytic steam reforming of the derived volatile products from the pyrolysis of wood sawdust, by using a fixed bed, two-stage reaction system. The aim was to enhance hydrogen production but minimize coke deposition on the reacted catalyst whilst maintaining catalyst stability.

2. Experimental

2.1. Preparation of materials and fresh catalysts

The properties of the raw materials (wood sawdust) utilized was presented in our previous report [7]. But briefly, the proximate analysis of the wood sawdust was 5.7 wt.% moisture, 74.8 wt.% volatiles, 18.3 wt.% fixed carbon, and 1.2 wt.% ash. The ultimate analysis showed that the wood sawdust was 5.9 wt.% hydrogen, 47.1 wt.% carbon, 0.1 wt.% nitrogen and 46.9 wt.% oxygen which was obtained by mass difference.

The NiO-ZnO-Al₂O₃ catalysts with different Ni molar ratios (5, 10, 15, 25, and 35%) and a constant Zn:Al molar ratio (Zn:Al=1:4) were prepared by a typical co-precipitation method [10, 52, 53]. Ni(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O (Sigma-Aldrich, Australia) were dissolved in deionized water to form a 1 mol L⁻¹ solution. The mixture of nitrated solutions with a Zn:Al molar ratio of 1:4 was precipitated using a 2 mol L⁻¹ NH₃·H₂O (Sigma-Aldrich, Australia) solution, adding drop by drop. When the pH of the suspension was around pH 8, the addition of ammonia solution was stopped. The suspension was then aged under agitation for one hour at 60 °C and filtered under vacuum. The obtained filter cake was dried in an oven at 80 °C for about 8 h. Finally, the precursor was calcined under an air atmosphere by heating the precursor to a temperature of 800 °C with a heating rate of 1 °C min⁻¹ and then held at 800 °C for 4 hours. The calcined fresh catalyst was ground into fine powder and sieved to obtain particle sizes with a range between 50 and 180 μm. The fresh NiZnAl catalysts were denoted as xNiZnAl where “x” indicates the nickel molar ratio (%), e.g. 5, 10, 15, 25 and 35.

2.2. Pyrolysis catalytic reforming of biomass

The prepared NiO-ZnO-Al₂O₃ catalysts were investigated for hydrogen production from the thermochemical conversion of biomass. A two-stage reactor was used in this work. In the first reactor, the wood sawdust was decomposed into pyrolysis vapours, which passed to the second reactor for catalytic steam reforming reactions for the production of hydrogen. The schematic diagram of the two-stage fixed bed reaction system was presented in our previous report [4].

For each experiment, N₂ was used as carrier gas with a flow rate of 80 ml min⁻¹. The wood sawdust sample (0.8 g) and fresh NiO-ZnO-Al₂O₃ catalyst (0.25 g) were placed in the first and second reactor, respectively. The temperature of the catalyst reactor was initially heated to 800 °C [54]. When the second reactor (catalyst bed) was stabilized at 800 °C, the first reactor where the biomass sample was located was heated to a temperature of 535 °C at a heating rate of 40 °C min⁻¹. Steam was generated by heating water, which was injected to the second reactor with a flow rate of 4.74 ml h⁻¹ using a syringe pump at the point when the pyrolysis reactor was started to be heated. In this work, sand was used instead of the catalyst for blank experiments.

The liquid product derived from the catalyst bed was collected with two condensers, which were air cooled and dry-ice cooled, respectively. A 25L TedlarTM gas bag was used to collect the non-condensed gases, which were further analyzed using off-line gas chromatograph (GC). The gas, residue yields and mass balance was calculated via the following Equations (1), (2) and (3), respectively:

$$\text{Gas Yield (wt.\%)} = \frac{\text{Gas mass}}{\text{Wood sawdust mass}} \times 100 \quad \text{Equation (1)}$$

$$\text{Residue Yield (wt.\%)} = \frac{\text{Residue mass}}{\text{Wood sawdust mass}} \times 100 \quad \text{Equation (2)}$$

$$\text{Mass balance (wt.\%)} = \frac{\text{Gas mass} + \text{Residue mass} + \text{Liquid mass} + \text{Char mass}}{\text{Wood sawdust mass} + \text{injected water mass}} \times 100 \quad \text{Equation (3)}$$

The mass of biomass char residue after pyrolysis was obtained by the mass difference of the sample boat before and after the experiment. The total reaction time for each experiment was about 40 minutes. Each catalyst was used only once for each experiment. The experiments reached a mass balance close to 100% which was used for verification of experimental accuracy and repeatability.

Selected experiments were repeated, for example, the standard deviations using the 35NiZnAl catalysts were: 0.69 for hydrogen yield, 2.27 for hydrogen concentration, 1.81 for CO₂ concentration and 0.18 for CH₄ concentration.

2.3. Characterization of gases

C₁ to C₄ hydrocarbons were analyzed with a Varian 3380 GC with a flame ionization detector (FID) and a HayeSep column (80-100 mesh) and carrier gas (N₂) were used. H₂, CO and N₂ were determined using a Varian 3380 GC with a molecular sieve column (60-80 mesh) and argon carrier gas. CO₂ gas was analyzed by another Varian 3380 GC on a HayeSep column (80-100 mesh) with carrier gas (argon).

2.4. Analysis of catalysts

N₂ adsorption isotherms (Quantachrome Autosorb-1) were used to obtain the specific surface area of the fresh NiO-ZnO-Al₂O₃ catalyst. Prior to the isotherm analysis, about 150 mg of catalyst was degassed under vacuum for 5h at 150 °C. The 5-point Brunauer, Emmett and Teller (BET) method was used to evaluate the surface area of the fresh catalyst. X-ray diffraction (XRD) patterns of the fresh catalysts were determined using a SIEMENS D5000 instrument using Cu K α radiation. The scanning range was between 10 and 70° and the scanning step was 0.02°. The crystal particle size (D) of the catalyst was obtained using Scherrer's formula (Equation (4)).

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad \text{Equation (4)}$$

where τ is the mean size of crystal particles; K is dimensionless shape factor; λ is the X-ray wavelength; β is the line broadening at half the maximum intensity; and θ is the Bragg angle.

The morphologies of the catalysts were analyzed by a scanning electron microscope (SEM) (LEO 1530). In addition, transmission Electron microscopy (TEM) (Phillips CM120 BioFilter) analysis was carried out to obtain detailed information about the fresh NiO-ZnO-Al₂O₃ catalysts. The reducibility of the prepared fresh catalysts was analyzed by temperature programmed reduction (TPR) using a thermogravimetric analyzer (SDT Q600). During the TPR analysis, about

15 mg fresh NiO-ZnO-Al₂O₃ catalyst was used. The catalyst sample was heated from room temperature to about 1200 °C at 10 °C min⁻¹ using 15 vol.% H₂ gas balanced with 85 vol.% N₂ (total flow rate was 100 mL min⁻¹).

3. Results and Discussion

3.1. Characterizations of the fresh NiZnAl catalysts

3.1.1. N₂ adsorption and XRD analysis of fresh NiO-ZnO-Al₂O₃ catalysts

Textural properties, theoretical metal composition and BET surface area of the fresh catalysts are shown in Table 1. The specific surface area of the fresh catalysts were 83.2 - 95.7 m² g⁻¹. It seems that increasing the Ni molar ratio from 5 to 35% did not significantly change the surface areas of the catalysts. XRD patterns of the fresh NiO-ZnO-Al₂O₃ catalysts are shown in Fig. 1, and the particle size of crystals in the NiO-ZnO-Al₂O₃ calculated from the XRD analysis are summarized in Table 1. It has been found that a ZnAl₂O₄ spinel structure was easily formed compared to NiAl₂O₄ spinel when the ions of Zn²⁺, Al³⁺ and Ni²⁺ coexisted inside the NiO-ZnO-Al₂O₃ catalyst, because Zn²⁺ ions can easily enter into the tetrahedral sites of the interstices between O²⁻ ions, while Ni²⁺ ions are difficult to enter into the close-packed O²⁻ ionic lattice [55]. From the XRD results, the presence of a spinel ZnAl₂O₄ phase (JCPDS 05-0669), characterized by two intense and symmetric peaks at 2θ=31.3° and 36.9° and other less intense peaks at higher 2θ values (2θ=59.4°, 65.3°), was clearly evidenced in all the fresh NiO-ZnO-Al₂O₃ catalysts, which is consistent with the results reported by Barroso et al. [3]. Meanwhile, the peak at 2θ=65.3° for stoichiometric NiAl₂O₄ spinel was displayed in all XRD patterns of fresh catalysts, the other peaks for the NiAl₂O₄ spinel phase which occur at values of approximately 2θ=19.1°, 31.4°, 37.0°, 45.0°, 55.9°, 59.6° also appeared distinctly (JCPDS 78-0552) [56]. A small crystal size (6-7 nm) of the spinel was calculated based on the Scherrer equation (Eq.(4)).

Based on the study of Buitrago-Sierra et al. [41], the most intense diffraction peak of ZnO at around 36.8° overlaps with the most intense ZnAl₂O₄ diffraction peak. A diffraction peak at 34.8° is assigned to discrete ZnO. However, in this work, there was no evidence to show the presence of ZnO in the fresh NiO-ZnO-Al₂O₃ catalysts. This effect may be due to the fact that ZnO

has completely reacted with Al_2O_3 upon calcination to form the ZnAl_2O_4 spinel phase. Meanwhile, the presence of Al_2O_3 was not obtained, which may be because the amount of remaining Al_2O_3 was too small to be detected [41] or due to the fact that $\gamma\text{-Al}_2\text{O}_3$ has poor crystallinity [3]. Furthermore, according to Buitrago-Sierra et al. [57], XRD typically detects crystallites that are larger than 2-5 nm; thus, it is possible that ZnO, NiO and Al_2O_3 exist on these catalysts have crystallite sizes smaller than the detection limit [56].

With increasing Ni molar ratio to 15%, the appearance of NiO was still not identified, which may be due to more NiAl_2O_4 spinel formation or the size/amount of remaining NiO was too small to be detected by XRD [41]. Further increasing the Ni molar ratio to 25%, and 35%, the diffraction peaks for NiO at values of approximately $2\theta=43.3^\circ$ and 62.9° (JDPDS 89-7131) were clearly evidenced and the main peak for NiO at the value of $2\theta=37.0^\circ$ may overlap with the peak of NiAl_2O_4 (JCPDS 78-1601) at the similar position of 2θ values [41, 56, 58].

ZnAl_2O_4 , NiAl_2O_4 phases with a crystallite size of approximate 6-7 nm, which were calculated based on the Scherrer equation, were assigned in the XRD patterns for all fresh NiO-ZnO- Al_2O_3 catalysts. In addition, NiO phases with a particle size of approximate 7 nm were identified in the XRD patterns for fresh NiO-ZnO- Al_2O_3 catalysts with a Ni molar ratio of 25% and 35%. The ZnAl_2O_4 , NiAl_2O_4 and NiO particle sizes were calculated based on ZnAl_2O_4 , NiAl_2O_4 and NiO diffraction peaks at the same 2θ value of 37.0° in the XRD patterns for all fresh NiO-ZnO- Al_2O_3 catalysts.

3.1.2. SEM and TEM analysis of the fresh NiZnAl

SEM images of the fresh NiO-ZnO- Al_2O_3 catalysts are shown in Fig. 2 to characterize the morphology of the catalysts. Increasing the Ni molar ratio from 5% to 15%, produced very similar morphologies (Fig. 2(a), (b) and (c)). The micrographs which can be seen from Fig. 2(a), (b), and (c) show the presence of agglomerates composed of small quasi-spherical particles in the micrometric scale. Further increasing the Ni molar ratio to 25% and 35%, resulted in more metal oxide particles being dispersed on the surface until clusters were formed (Fig. 2(d) and Fig. 2(e)). From Fig. 2(d) and Fig. 2(e), the metal oxide clusters are densely dispersed on the surface, and it is difficult to differentiate ZnAl_2O_4 , NiAl_2O_4 and NiO particles which have been identified from XRD (Fig. 1).

The TEM images of the fresh 5NiZnAl and 35NiZnAl catalysts at scales of 20 nm and 50

nm are depicted in Fig. 3. From Fig. 3., a high dispersion of the metal oxide particles can be observed. The particle size obtained from TEM images was around 6-7 nm which is consistent with the XRD results as shown in Table 1 for the 5NiZnAl and the 35NiZnAl catalysts. From the XRD, SEM and TEM analysis of the fresh catalysts, it is suggested that nano-metal particles are successfully dispersed on the surface of the NiO-ZnO-Al₂O₃ catalysts, indicating a high dispersion of metal particles was obtained.

3.1.3. TPR analysis of fresh NiZnAl catalysts

The TPR analysis of the fresh catalyst was performed to study the reduction properties of surface metal oxide compounds on the fresh catalysts. As shown in Fig. 4, for the fresh 5NiZnAl and 10NiZnAl catalysts, a broad hydrogen consumption band was obtained between 650 and 1050 °C with a maximum consumption at around 1000 °C, and these can be assigned to the reductions of ZnAl₂O₄ and NiAl₂O₄ spinel phases [59-61]. High temperature was required to reduce the fresh catalyst; it is suggested that this was due to the strong interactions between metals and catalyst support [56].

When the Ni molar ratio was increased to 15%, an extra reduction peak was observed at around 830 °C, in relation to the reduction of stoichiometric NiAl₂O₄ spinel phase [56, 62]. When the Ni molar ratio was further increased to 25% and 35%, a reduction peak at around 500 °C can be related to the reduction of NiO [56]. Ni content has been reported to dissolve preferably with Al₂O₃ support at high temperature to form NiAl₂O₄ spinel phase when Ni loading was low; with the increase of Ni content, bulk NiO particles were formed [58, 62].

It is noted that for all the fresh catalysts, the reduction temperature of ZnAl₂O₄ or NiAl₂O₄ changed from around 1000 to 900 °C with increasing Ni content. This result is consistent with the literature investigating catalysts prepared by sol-gel and co-precipitation [60, 61, 63, 64]. For example, Guo et al. [63] investigated nickel catalysts with MgAl₂O₄ spinel as support using TPR analysis and two reduction peaks were found; the maximum reduction temperature of the second peak moved from 800 to 705 °C with the increase of Ni loading from 1 to 15 wt.%.

3.2. Wood sawdust pyrolysis and catalytic reforming with NiO-ZnO-Al₂O₃ catalysts

3.2.1. Product yield

Gas and hydrogen production from the pyrolysis-catalytic steam reforming of wood sawdust is shown in Table 2. The residue yield stabilized at around 37.5 wt.% in this work since pyrolysis in the first stage reactor was the same for each experiment. Liquid products collected from the condensers consisted of a mixture of bio-oil and non-reacted water. The mass of the injected water into the reaction system was calculated by the weight difference of the syringe.

For the blank experiment using a sand bed, the gas yield in relation to the mass of wood sawdust was 33.0 wt.%, and the hydrogen production was 2.4 mmol H₂ g⁻¹ wood sawdust (Table 2). However, with the addition of NiO-ZnO-Al₂O₃ catalysts with Ni molar ratios ranging from 5 to 35%, both the gas and hydrogen yields were enhanced gradually and significantly, from 49.3 to 74.8 wt.% and from 8.2 to 20.1 mmol H₂ g⁻¹ wood sawdust, respectively. It indicates that the NiO-ZnO-Al₂O₃ catalyst is efficient for hydrogen production from pyrolysis catalytic reforming of wood sawdust.

ZnAl₂O₄ phases were reported to increase the production of hydrogen by the promotion of the water gas shift reaction, when steam reforming of ethanol was investigated using Ni/Al₂O₃ catalysts promoted by Zn [41]. The influence of Ni content on hydrogen production has been reported by other researchers. For example, Corujo et al. [31] investigated the catalytic activity of a Ni/Dolomite catalyst for the gasification of forestry residue in the presence of steam. They reported that the optimal result in terms of hydrogen production was found with the catalyst containing the smallest amount of NiO (0.4Ni/Dolomite). NiZnAl catalysts with different atomic ratios of Zn/Al (0-25 wt.% Ni amount) were used for ethanol steam reforming; high hydrogen production and selectivity were observed on the catalysts containing a nickel amount between 18 and 25 wt.% [3]. In our previous work [7], the pyrolysis and steam reforming of wood sawdust with a Ni/MCM-41 catalyst was studied. When the Ni content in the Ni/MCM-41 catalyst was increased from 5 to 40 wt.%, the gas production was increased from 40.7 to 62.8 wt.% and the H₂ yield was enhanced from 6.2 to 18.2 mmol H₂ g⁻¹ sample, respectively.

Smaller metal particle size and more catalytic active sites have been reported to enhance gas production from reforming reactions [3, 59, 65]. For example, in our previous work, for pyrolysis- catalytic steam reforming of biomass with Ni/MCM-41 catalyst [7], the production of hydrogen and gas was significantly increased with the increase of Ni loading from 5 to 20 wt.%

while NiO crystal size was stable (around 2.9 nm). However, with the further increase of Ni loading to 40 wt.%, gas and hydrogen showed slight changes; this was suggested to be due to the enlargement of NiO particles. In addition, ZnAl₂O₄ supported Pt catalysts applied in the n-butane dehydrogenation process was investigated [65]. The Pt catalysts with ZnAl₂O₄ prepared by a co-precipitation method presented high catalytic activity and product selectivity compared to the ZnAl₂O₄ catalysts prepared by mechano-chemical synthesis. This was due to the ZnAl₂O₄ catalyst prepared by the co-precipitation method exhibiting higher dispersion of metal particles.

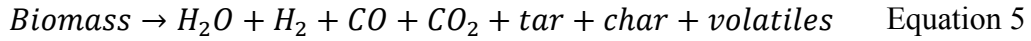
In this work, the average size of metal particles was about 6 nm, calculated from the XRD analysis (Table 1 and Fig.1). In addition, the metal particle size was maintained when the Ni content was increased from 5% to 35%. Therefore, higher yields of gas and hydrogen were obtained with the increase of catalytic sites during pyrolysis-catalytic steam reforming of wood sawdust in this work. Furthermore, TPR analysis also suggests that more catalytic sites were generated with the increase of Ni content from 5% to 35% as the catalyst becomes more reducible (Fig.4).

3.2.2. Gas concentration

In this work, the biomass was initially pyrolysed to produce H₂O, H₂, CO, CO₂, CH₄, tar, char and organic volatiles (Eq. (5)) in the first stage pyrolysis reactor, followed by the reforming of tar and organic volatiles in the second stage. The second stage includes reactions of CO, CO₂, H₂ and H₂O with the hydrocarbons and oxygenated compounds derived from pyrolysis of wood sawdust, thereby producing gaseous products. Nitrogen carrier gas was used throughout the experiments, and the gas fractions of the produced gases and the consequent reduction in nitrogen concentration (typically reduced to ~90 vol.%) in the collected gas sample bag were used for the determination of the mass of gases produced. In this work, the data reported in Table 2 is for the volume percent of each gas on a N₂ free basis.

The steam atmosphere and the utilization of catalyst promotes the decomposition and reforming reactions so that more light gases, such as H₂, CO, CH₄ and CO₂ are produced [66]. It is well known that the water-gas shift reaction (Eq.(6)), steam reforming of hydrocarbons and oxygenated compounds (Eq. (7) and Eq. (8)), CO₂ reforming of hydrocarbons and oxygenated compounds (Eq. (9) and Eq. (10)), decomposition reactions of hydrocarbons and oxygenated compounds, carbon gasification reaction (Eq. (13)) together with Boudouard reaction (Eq. (14)) were the main reactions which occurred in parallel and contributed to the high total gas and H₂

yields [67].



The gas composition for the non-condensed gas product after the catalytic steam reforming of derived products from pyrolysis of wood sawdust are listed in Table 2. CO, H₂, CO₂ and CH₄ were found to be the main gases from the non-catalytic steam reforming process with a sand bed (45.5 vol.% of CO, 17.4 vol.% of H₂, 14.5 vol.% of CO₂ and 14.8 vol.% of CH₄). Increasing the Ni content to 10%, the gas concentration showed a similar but not significant trend as increasing the Ni molar ratio from 0 to 5%. The CO, CH₄ and C₂-C₄ concentrations slightly decreased from 33.8 to 32.7 vol.%, from 10.2 to 8.9 vol.% and from 2.4 to 1.3 vol.%, respectively. While the H₂ content increased from 34.7 to 38.1 vol.% with a similar amount of CO₂ (from 18.9 to 19.0 vol.%). Both the water gas shift reaction and dry reforming contributed to the process. Further increasing the Ni molar ratio to 15%, the H₂ concentration increased continuously from 32.7 to 37.3 vol.% and the CH₄ content was diminished from 8.9 to 6.3 vol.%. However, the CO concentration increased from 32.7 to 37.3 vol.%, CO₂ content was consumed from 19.0 to 16.2 vol.% with the similar C₂-C₄ concentration (from 1.3 to 1.5 vol.%), which might be attributed to the CO₂ dry reforming with methane (Eq.(13)). With the increase of the Ni molar ratio continuously from 15% to 25%, the H₂ content increased significantly from 38.7 to 46.9 vol.%, CH₄ and C₂-C₄ concentration were decreased from 6.3 to 0.9 vol.% and from 1.5 to 0.2 vol.%, respectively, with the similar reductions for CO (from 37.3 to 36.7vol.%) and CO₂ amount (from 16.2 to 15.3 vol.%). Obviously, steam reforming of hydrocarbons mainly contributed to the process. The produced CO

should be consumed by the water-gas shift reaction (Eq.(6)). The amount of CO₂ would be balanced after dry reforming of hydrocarbons, which has been promoted by the increased Ni catalytic active sites.

When the Ni molar ratio was increased to 35%, the H₂ concentration was enhanced continuously from 46.9 to 48.1 vol.%, the CO content in the total gas remained constant at around 36.7 vol.%, and CO₂, CH₄ and C₂-C₄ concentration were all slightly decreased, from 15.3 to 15.1 vol.%, from 0.9 to 0.2 vol.% and from 0.2 to <0.1 vol.%, respectively, which indicates that the major reactions which occurred were CO₂ reforming and decomposition reactions of hydrocarbons and oxygenated compounds via Eq. (7)-(10). Similar changes of the gas composition were reported based on the work of Barroso et al. [3] that the H₂ concentration increased while the CH₄ and C₂-C₄ concentrations decreased with the increase of Ni content during the ethanol steam reforming on a NiZnAl catalyst prepared by incipient wet impregnation method.

According to the gas composition data in Table 2, the highest total gas and H₂ yields were obtained from the steam reforming process carried out with the 35NiZn4Al catalyst, the highest H₂/CO ratio was obtained with 25NiZn4Al and 35NiZn4Al catalysts, while the lowest the CO/CO₂ ratio was obtained with the utilization of 10NiZn4Al catalyst.

The gas composition performance of biomass catalytic steam gasification has also been studied by other researchers [1, 31, 40, 66]. Among the aforementioned reports for investigating the influence of Ni loading on gas concentrations during steam reforming of hydrocarbons, it was found that H₂ was increased and concentrations of CH₄ and C₂-C₄ were reduced. However, changes of CO and CO₂ concentrations could be different since CO and CO₂ were produced and consumed in parallel based on Eq. (7)-(11). For example, Corujo et al. [31] reported that CO concentration was increased and CO₂ concentration was decreased with the increase of Ni loading from 0.4 to 4.3 wt.% of Ni/Dolomite catalysts during the steam gasification of forestry residue. While we have reported different trends for CO and CO₂ gases found from the pyrolysis-catalytic steam reforming steam of biomass in the presence of Ni/MCM-41 catalysts with a Ni loading ranging from 5 to 40 wt.% [7], which is consistent with the promotion of the water-gas shift reaction (Eq. (6)).

3.3. Investigation of coke deposition on the reacted catalysts

TPO analysis was carried out on the reacted catalysts and the results are depicted in Figure

5 via weight change versus temperature. Two oxidation stages in the TPO analysis are shown in Figure 5, metal particle oxidation and carbon oxidation. The peaks of increasing mass from 250 to 500 °C and above 700 °C were assigned to the oxidation of Ni, Zn and other reduced metal species during the TPO analysis. The reduced metal species are suggested to be produced during the pyrolysis and gasification process where the reduction agents, H₂ and CO, were present and therefore the fresh catalysts did not need to be reduced before gasification experiments [7].

The weight loss before 550 °C for the TPO analysis might be assigned to the oxidation of amorphous carbons. The oxidation peak at a higher temperature which starts from 550 to 700 °C might be attributed to the oxidation of carbon deposited on the catalyst surface, probably filamentous carbon [68, 69]. The amount of coke formation on the catalyst was obtained from the weight loss of catalyst during the TPO analysis divided by the initial sample weight. In addition, it should be noted that the weight increase in Figure 5 was ascribed to the oxidation of metallic sites (Ni), which was produced during the reaction. In this work, the weight increase was not included for the calculation of coke formation. It is demonstrated from Figure 5 that the total amount of coke deposition was 0.1 wt.% of the used NiO-ZnO-Al₂O₃ catalyst with a Ni molar ratio of 35%, which can be considered as negligible indicating that coke resistant catalysts have been obtained after adding Zn during the synthesis in this work. Corujo et al. [31] reported more than 5 wt.% amount of coke formation on a Ni/dolomite catalyst for the 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. [24].

The presence of amorphous and filamentous carbons (“whiskers”) on the surface of the reacted catalysts was also confirmed by SEM analysis, shown in Figure 6. However, due to the low amount of carbon deposition, the appearance of filamentous carbon cannot be observed clearly in the TEM analysis image shown in Figure 7. The filamentous carbons had a diameter of between 10-20 nm, which is believed to be related to the metal particle size [68, 69].

According to the catalyst coke deposition data listed in Table 2, when the Ni content is in the range from 5% to 15%, the amount of coke deposition is approximately the same. Further increasing the Ni content to 25% and 35%, the coke deposition on the catalyst declined to a significantly low level (<1wt.%). Based on the work of Sutton et al. [21], for a Ni based Al₂O₃ catalysts applied to the biomass gasification process, due the acidic character of the Al₂O₃ support and the easy sintering property of Ni metal, with the increase of Ni content, the amount of coke

deposition displayed an increasing trend. However, in this work, with the addition of promoter Zn, the coke deposition appeared as a decreasing trend with the increase of Ni content in the catalysts. This indicated the addition of promoter metal Zn has the advantage of suppressing the coke deposition on the catalyst, which helps increase the thermal stability and lifetime of the catalyst.

4. Conclusions

In this work, NiO-ZnO-Al₂O₃ catalysts with different Ni content and a constant Zn:Al molar ratio of 1:4 prepared by a co-precipitation method have been investigated for the production of a hydrogen-rich syngas from the thermochemical conversion of biomass in the form of wood sawdust. The process involved pyrolysis of the biomass followed by catalytic steam reforming of the evolved pyrolysis volatiles in the presence of the NiO-ZnO-Al₂O₃ catalyst with different Ni loadings.. It was found that the NiO-ZnO-Al₂O₃ catalysts prepared by the co-precipitation method had well-dispersed NiO, ZnAl₂O₄ and NiAl₂O₄ crystal phases with a particle size of approximate 6-7 nm. Gas production was increased from 49.3 to 74.8 wt.% and the H₂ yield was enhanced from 8.2 to 20.1 mmol g⁻¹ wood sawdust with the increase of Ni molar ratio from 5 to 35% in the prepared catalyst. The enhanced hydrogen production with the increase of Ni content was suggested to be due to the increased number of catalytic sites (mainly Ni metal based on the XRD and TPR analysis). While the particle size of metal crystals was not changed significantly with the increase of Ni content due to the promoting effect of ZnO. In addition, with the increase of Ni content and the addition of the promoter metal Zn, the coke deposition displayed a decreasing trend. When the Ni content was increased to 25 and 35%, the coke deposition on the used catalyst was negligible (<1 wt.%).

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Table 1

Theoretical metal composition, particle size and BET surface area of fresh catalysts

Sample	Theoretical Metal Composition (wt.%) ^a			Particle size(nm) (Obtained from XRD data)			BET surface area(m ² g ⁻¹)
	Ni	Zn	Al	ZnAl ₂ O ₄	NiAl ₂ O ₄	NiO	
5NiZn4Al	5.1	21.4	35.4	11	11	-	88.5
10NiZn4Al	10.0	20.0	33.0	11	11	-	89.7
15NiZn4Al	14.7	18.6	30.7	11	11	-	83.2
25NiZn4Al	23.9	16.0	26.3	11	12	12	84.3
35NiZn4Al	32.5	13.4	22.2	11	12	12	95.7

^a Theoretical metal composition was calculated by the amount of metal divided by the amount of all the metal oxides, like the theoretical Ni composition equals Ni/(NiO+ZnO+Al₂O₃) (wt.%)

Table 2

Mass balance and gas compositions from pyrolysis and steam reforming of wood sawdust in the presence of NiZnAl catalysts with different Ni molar ratios

Catalytic bed	Sand	5NiZnAl	10NiZnAl	15NiZn4Al	25NiZnAl	35NiZnAl
Gas/Wood (wt.%)	33.0	49.3	51.7	60.8	65.6	74.8
Residue/Wood (wt.%)	38.8	37.5	37.5	37.5	37.5	36.3
H ₂ Yield (mmol H ₂ g ⁻¹ sample)	2.4	8.2	9.8	11.8	16.9	20.1
Coke deposition (wt.%)	-	2.2	1.7	2.1	0.2	0.1
Gas Composition (Vol.% N ₂ free)						
CO	45.5	33.8	32.7	37.3	36.7	36.7
H ₂	17.4	34.7	38.1	38.7	46.9	48.1
CO ₂	14.5	18.9	19.0	16.2	15.3	15.1
CH ₄	14.8	10.2	8.9	6.3	0.9	0.2
C ₂ -C ₄	7.8	2.4	1.3	1.5	0.2	0.0

FIGURE CAPTIONS

Fig. 1. XRD analysis results of the fresh NiZnAl catalysts; (a): 5NiZn4Al; (b): 10NiZn4Al; (c): 15NiZn4Al; (d): 25NiZn4Al; (e): 35NiZn4Al

Fig. 2. SEM results of the fresh NiZnAl catalysts

Fig. 3. TEM results of the fresh NiZnAl catalysts

Fig. 4. TPR results of the fresh NiZnAl catalysts; (a): 5NiZnAl; (b): 10NiZnAl; (c): 15NiZnAl; (d): 25NiZnAl; (e): 35NiZnAl

Fig. 5. TPO results of the reacted NiZnAl catalysts; (a): reacted 5NiZnAl; (b): reacted 10NiZnAl; (c): reacted 15NiZnAl; (d): reacted 25NiZnAl; (e): reacted 35NiZnAl

Fig. 6. SEM results of the reacted NiO-ZnO-Al₂O₃ catalysts

Fig. 7. TEM results of the reacted NiO-ZnO-Al₂O₃ catalysts with a Ni molar ratio of 15%

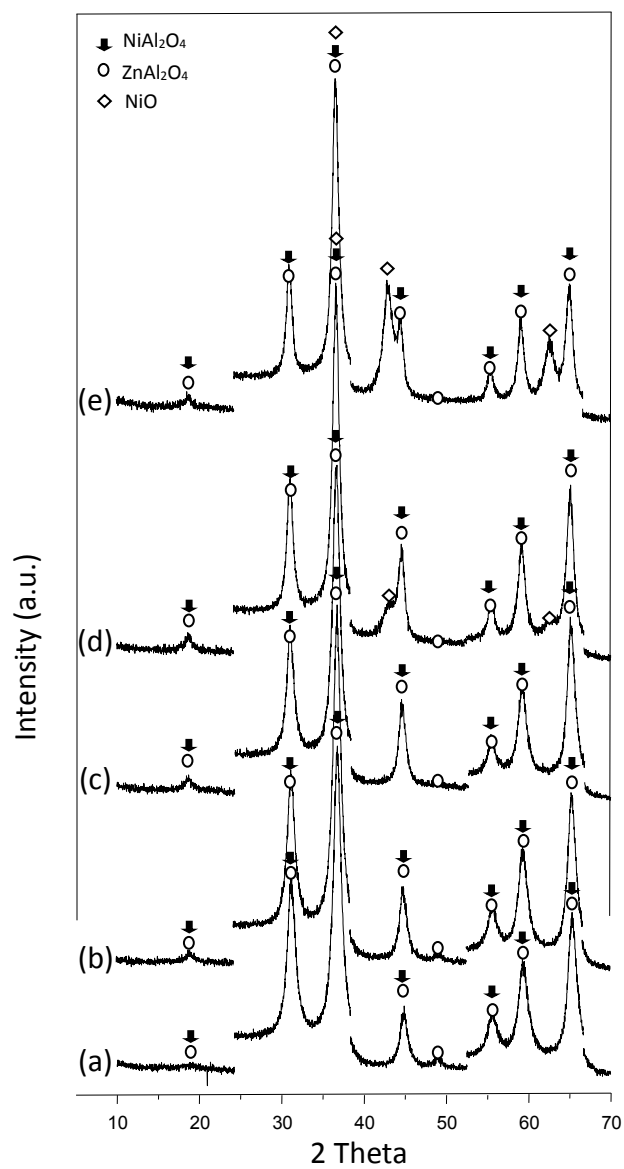
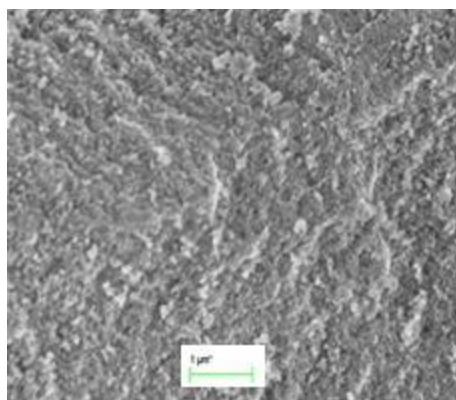
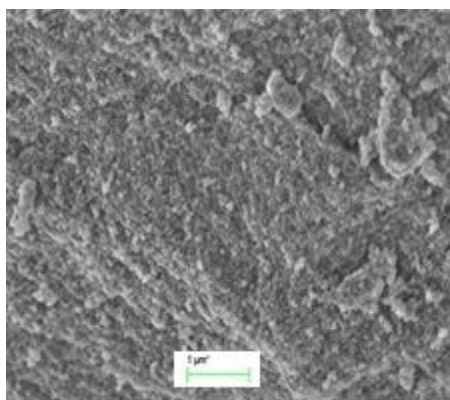


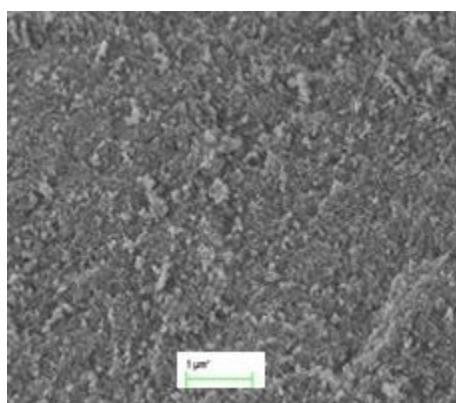
Figure 1 XRD analysis results of the fresh NiZnAl catalysts; (a): 5NiZn4Al; (b): 10NiZn4Al; (c): 15NiZn4Al; (d): 25NiZn4Al; (e): 35NiZn4Al



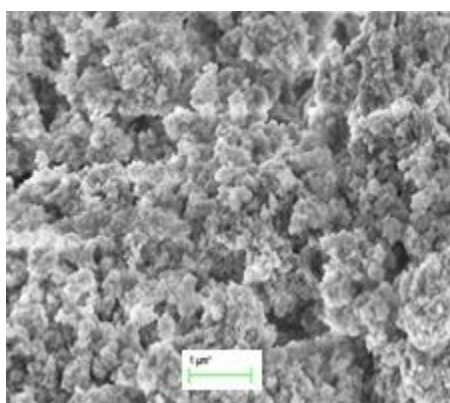
(a) 5NiZnAl catalyst



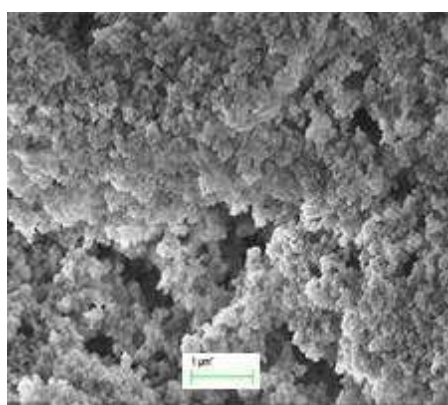
(b) 10NiZnAl catalyst



(c) 15NiZnAl catalyst

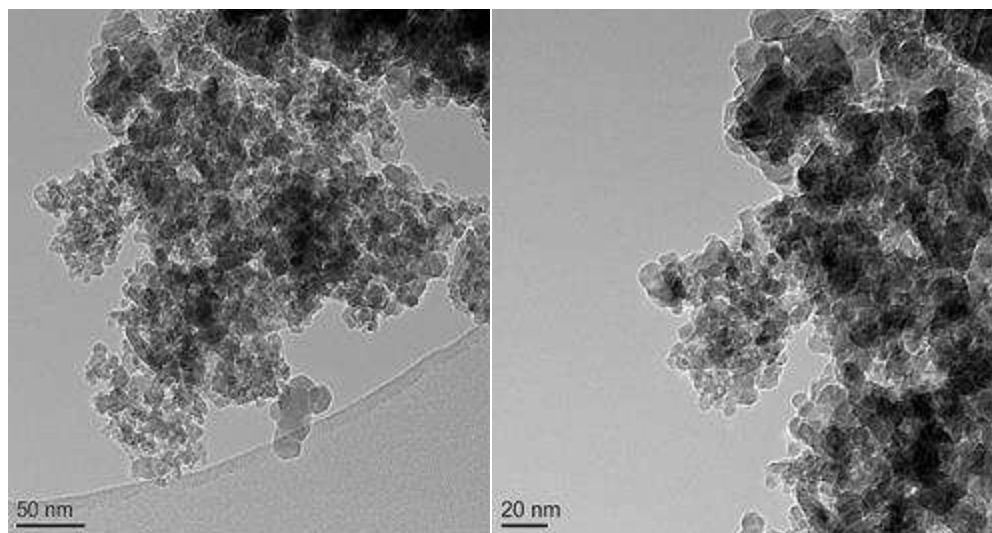


(d) 25NiZnAl catalyst

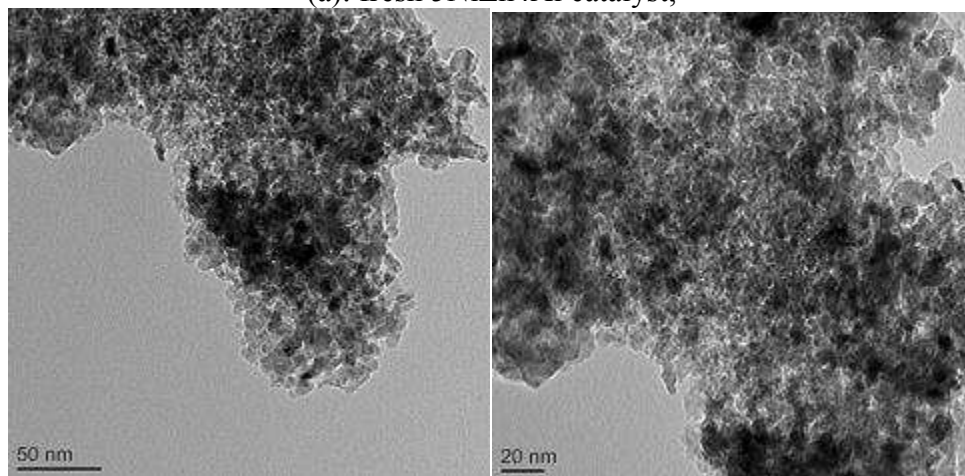


(e) 35NiZnAl catalyst.

Figure 2 SEM results of the fresh NiZnAl catalysts



(a): fresh 5NiZn4Al catalyst;



(b): fresh 35NiZn4Al catalyst.

Figure 3 TEM results of the fresh NiZnAl catalysts

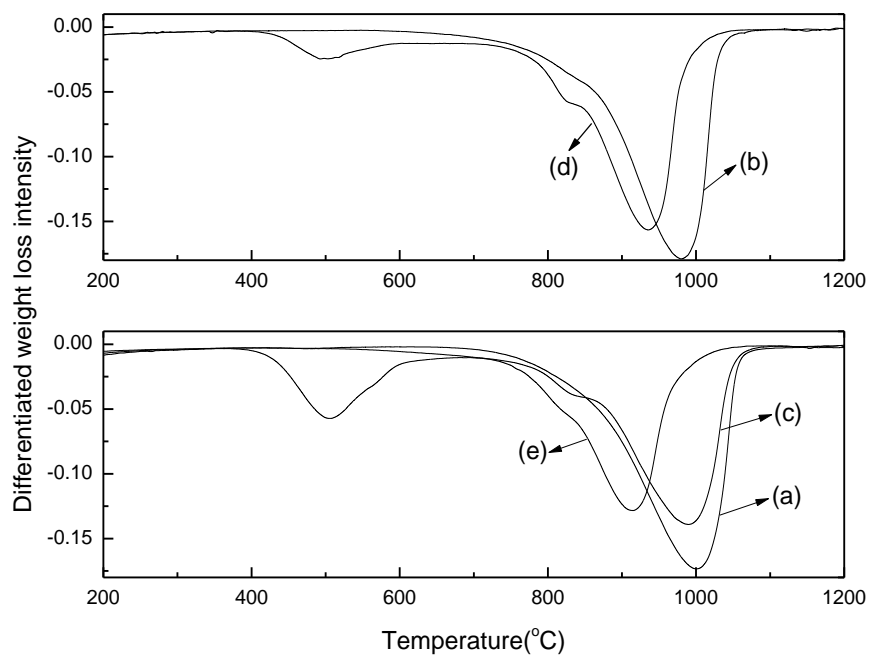


Figure 4 TPR results of the fresh NiZnAl catalysts; (a): 5NiZnAl; (b): 10NiZnAl; (c): 15NiZnAl; (d): 25NiZnAl; (e): 35NiZnAl

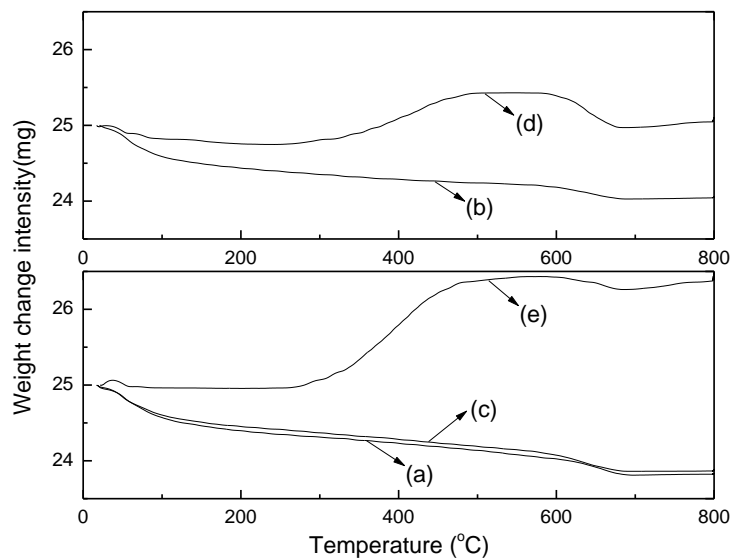
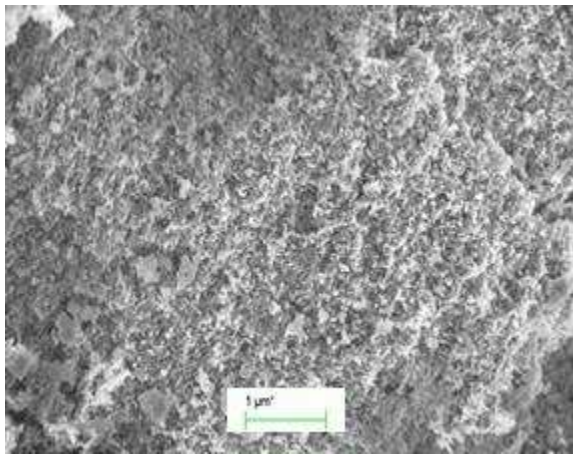
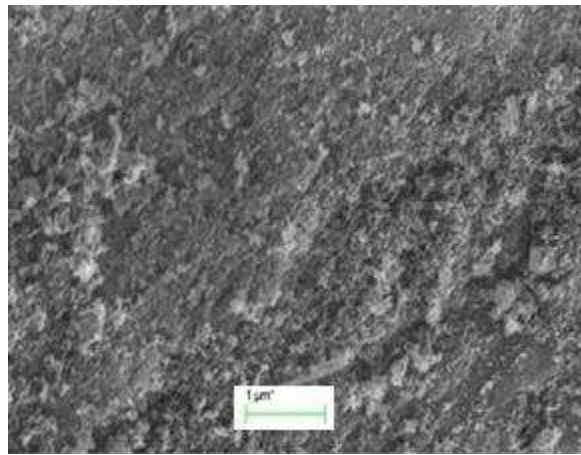


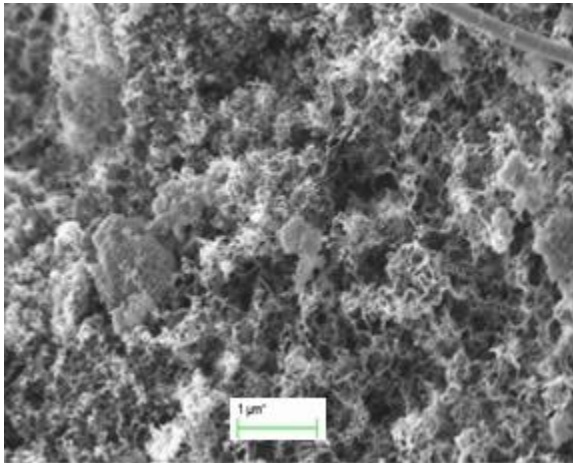
Figure 5 TPO results of the reacted NiZnAl catalysts; (a): reacted 5NiZnAl; (b): reacted 10NiZnAl; (c): reacted 15NiZnAl; (d): reacted 25NiZnAl; (e): reacted 35NiZnAl



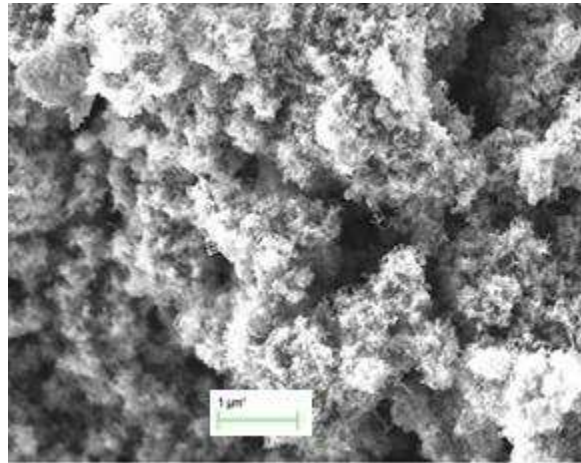
(a) 5NiZnAl



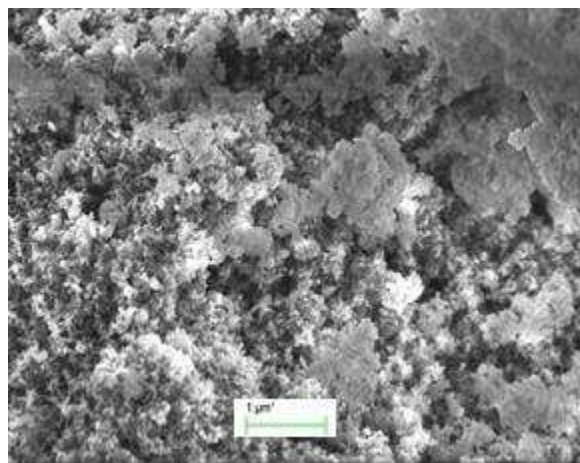
(b) 10NiZnAl



(c) 15NiZnAl



(d) 25NiZnAl



(e): 35NiZn4Al

Figure 6 SEM results of the reacted NiO-ZnO-Al₂O₃ catalysts

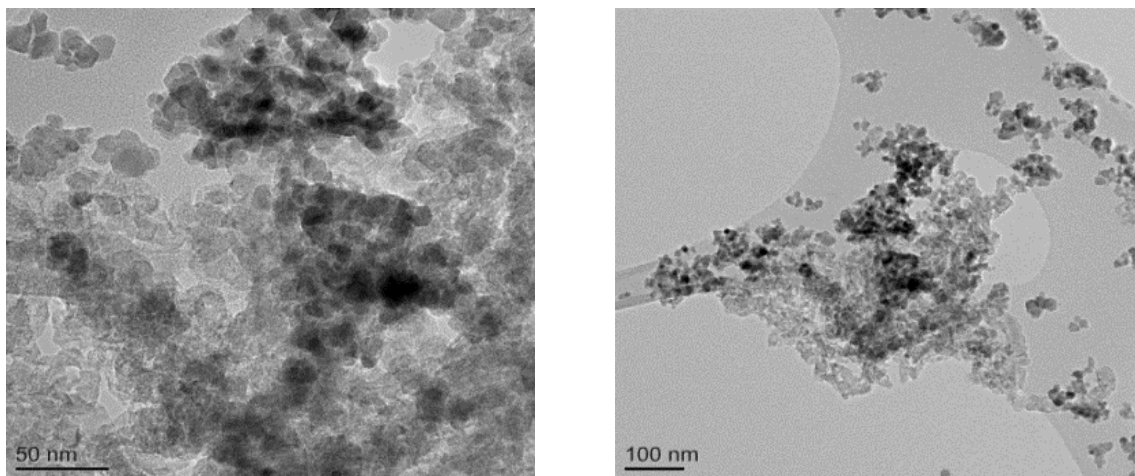


Figure 7: TEM results of the reacted NiO-ZnO-Al₂O₃ catalysts with a Ni molar ratio of 15%