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Wu, C, Wang, Z, Wang, L et al. (2 more authors) (2014) Catalytic steam gasification of biomass for a sustainable hydrogen future: influence of catalyst composition. Waste and Biomass Valorization, 5 (2). 175 - 180. ISSN 1877-2641

https://doi.org/10.1007/s12649-013-9244-9

Catalytic steam gasification of biomass for a sustainable hydrogen future: Influence of catalyst composition

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Abstract

Hydrogen is regarded as a clean energy for fuelling the future. Hydrogen will be the energy carrier from other resources such as hydropower, wind, solar and biomass. Producing hydrogen from gasification of biomass wastes, particularly in the presence of steam, represents a promising route to produce this clean and CO_2-neutral fuel. The steam pyrolysis-gasification of biomass (wood sawdust) was carried out with various nickel-based catalysts for hydrogen production in a two-stage fixed bed reaction system. The wood sawdust was pyrolysed in the first reactor and the derived products were gasified in the second reactor in the presence of the catalyst and steam. The synthesised Ni-Ca-Al and Ni-Zn-Al catalysts were prepared by co-precipitation method with different Ni loadings of 20 mol.% and various Zn/Al or Ca/Al ratios, which were characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM) and temperature-programmed oxidation (TPO). The results showed that the Ni/Zn-Al (1:9) catalyst resulted in higher hydrogen production (23.9 mmol H_2 g^{-1} biomass) compared with the Ni/Ca-Al (1:9) catalyst (12.7 23.9 mmol H_2 g^{-1} biomass) and in addition, the increase of Ca or Zn content in the catalyst slightly increased the hydrogen production. The TPO results showed that the catalyst suffered negligible coke deposition from the catalytic steam pyrolysis/gasification of wood sawdust. Additionally, Na_2CO_3 catalyst preparation agent was also found to produce a catalyst with better performance and lower coke deposition, compared with NH_4OH catalyst preparation agent, as observed by TPO, SEM and TEM analysis.

Keywords: Biomass, Pyrolysis, Gasification, Nickel, Hydrogen

1. Introduction

Hydrogen production from biomass gasification has drawn significant attention recently, since biomass is regarded as a carbon-neutral renewable feedstock material and hydrogen is seen as one of the most important energy carriers in the future [1,2]. By using biomass to produce energy and fuels from the gasification process, the influence of greenhouse gases on climate change could be reduced and a country's energy security could be improved by reducing the dependence on imported fossil fuels.

Extensive investigations have been carried out to screen suitable catalysts for hydrogen production from biomass gasification [1,3]. Among them, Ni-based catalysts have been reported as one of the most promising catalysts [4,5], since nickel-based catalyst are effective and comparatively cheaper compared with noble metal catalysts.

Co-precipitation as a preparation method for catalysts has been reported for the preparation of Ni-Al catalysts, which have been widely used in the gasification of biomass and other hydrocarbon materials [6,7]. Additionally, metals such as Ca have been added to the Ni-Al catalyst system to improve the catalytic performance such as the enhancement of hydrogen production and the prohibition of coke deposition during the gasification process [8,9].

In this work, various Ni-based catalysts were prepared by a co-precipitation method and were applied in the pyrolysis-gasification of wood sawdust. The purpose was to obtain the influence of methods of catalyst composition and preparation such as adding metals Zn or Ca and preparation agents such as NH_4OH or Na_2CO_3 on the hydrogen production and coke deposition from the gasification process.

2. Experimental

2.1 Materials

Wood sawdust (less than 0.2 mm) was used in this work. The elemental analysis and proximate analysis were carried out and showed a moisture content of 6.4 wt.%, volatile content of 74.8 wt.%, fixed carbon of 18.3 wt.% and an ash content of 1.2 wt.%; in addition, C, H, O and N content was 47.1, 5.9, 46.9 and 0.1 wt.%, respectively, from the elemental analysis.

The catalysts were prepared by a co-precipitation method with the initial Ni-loading mole ratio was 20 mol.%. $Ni(NO_3)_3{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, NH_4OH and Na_2CO_3 were purchased from Sigma–Aldrich. Precursors with desired Ni/ZnAl (1:9) (Zn/Al molar ratio 1:9), Ni/ZnAl (1:1) (Zn/Al molar ratio 1:1), Ni/CaAl (Ca/Al molar ratio 1:9) were prepared by dissolving metal salts in deionized water. The precursor mixture was precipitated with the basic solution of NH_4OH or Na_2CO_3 in order to adjust the pH of the suspension between 6 and 9. After precipitation, the suspension was aged under agitation for an hour and then filtered under vacuum. The filter cake obtained was rinsed with deionized water, followed by drying at 80 °C overnight. Finally, the solids were calcined at 800 °C for 4h with a heating rate of 1 °C min^{-1} in static air.

2.2 Experimental system and analysis methods

A schematic diagram of the reactor system has been reported in our previous work [10]. 0.8 g wood sample and 0.5 g catalyst were used in each experiment. Water was injected with a flow rate of 4.74 g h^{-1}, while carrier gas N_2 flow rate was 80 ml min^{-1}. Gasification temperature was fixed at 800 °C; then the pyrolysis reactor was started to be heated to 500 °C with a heating rate of 40 °C min^{-1}; in the meantime, water was injected. The experiment was found to be almost completed with a total time of 40 min after starting heating the first reactor (pyrolysis). The generated products from the second reactor were condensed with an air-cooled condenser and a dry-ice cooled condenser. The non-condensed gases were collected by a 25 L Tedlar^{TM} gas bag.

The BET (Brunauer, Emmett and Teller) surface area of the fresh catalysts was determined using a NONA 2200e Surface Area and Pore Size Analyzer. The BET surface area for the Ni/CaAl (1:9)-NH_4OH, Ni/ZnAl (1:9)-NH_4OH, Ni/ZnAl (1:1)-NH_4OH and Ni/CaAl (1:9)-Na_2CO_3 are 79.7, 141.7, 43.1 and 54.7 m^2 g^{-1}, respectively.

X-ray diffraction (XRD) analysis was carried out to the prepared fresh catalysts using a SIEMENS D5000 in the range of 10-70° with a scanning step of 0.02° using Cu Kα radiation.

Scanning electron microscopy (SEM) (LEO 1530) coupled to an energy dispersive X-ray spectroscope (EDXS) was used to characterize the used catalysts.

The temperature-programmed oxidation (TPO) of the reacted catalysts was carried out using a Stanton-Redcroft thermogravimetric analyser (TGA and DTG) to determine the properties of the coked carbons deposited on the reacted catalysts. About 10 mg of the reacted catalyst was heated in an atmosphere of air at 15 °C min^{-1} to a final temperature of 800 °C, with a dwell time of 10 minutes.

Temperature programmed reduction (TPR) was use to characterize the fresh catalysts. The TPR was carried out using the above TGA under the atmosphere of hydrogen gas (5 vol.% H_2 balanced with N_2) heated up to 150 °C with holding time 30 min, then heated up to 900 °C with the heating rate of 10 °C min^{-1}.

Transmission electron microscopy (TEM) (Philips CM200) coupled with EDXS was used to determine the reacted Ni/CaAl and Ni/ZnAl catalyst.

3. Results and discussion

3.1. Product yield and gas concentrations

Catalytic steam pyrolysis-gasification experiments were conducted with Ni/CaAl (1:9)-NH_4OH, Ni/ZnAl (1:9)-NH_4OH, Ni/ZnAl (1:1)-NH_4OH and Ni/CaAl (1:9)-Na_2CO_3 catalysts. The experimental results are shown in Table 1. After pyrolysis on above catalysts, the residue of the biomass sample was around 30 wt.% of the original sample weight, and gas production was higher than 60 wt.% related to the weight of biomass sample. The presence of catalyst has shown obvious improvement for hydrogen production compared with the non-catalytic pyrolysis/gasification of wood biomass [10] where only 5.6 mmol H_2 g^{-1} biomass and 31.1 Vol.% of H_2 concentration were obtained, respectively. Among the investigated catalysts, gas and hydrogen productions were lower for the Ni/CaAl (1:9) catalyst, compared with the Zn-doped catalysts. For example, the gas yield was around 63.5 wt.% for the pyrolysis/gasification of wood sawdust in the presence of the Ni/CaAl (1:9)-NH_4OH catalyst; while the gas yield was higher than 70 wt.% for the Ni/ZnAl catalyst with a Zn/Al ratio of 1:9 and 1:1.

Additionally, hydrogen production from the Ni/CaAl catalysts was also lower than the Ni/ZnAl catalysts. In Table 1, 12.7 and 17.8 mmol H_2 g^{-1} biomass was obtained for the catalytic pyrolysis/gasification of sawdust in the presence of the Ni/CaAl (1:9)-NH_4OH and Ni/CaAl (1:9)-NH_4OH catalyst, respectively. The hydrogen production with the Ni/ZnAl catalyst was higher than 20 mmol H_2 g^{-1} biomass sample.

As shown in Table 1, the catalytic pyrolysis/gasification of wood sawdust generates low concentration of hydrocarbon gases. Less than 6 vol.% of CH_4 and lower than 2.1 Vol.% of C_2-C_4 hydrocarbons were obtained. The Ni/Zn-Al catalyst produced less hydrocarbon gases compared with the Ni/Ca-Al catalyst (Table 1). Higher concentration of H_2 (around 55 Vol.%) was also obtained from the catalytic pyrolysis/gasification process with the Ni/ZnAl catalysts, while only 41.4 Vol.% of H_2 concentration was obtained for the Ni/CaAl (1:9)-NH_4OH catalyst. Ni-Ca-Al catalyst has been used for the hydrogen production from catalytic steam reforming of biomass pyrolysis liquids [11]; Ca was proposed to lower the H_2/CO ratio during the experiment. Zn metal has been reported to have good performance related to the improvement of hydrogen production from ethanol steam reforming [12,13].

The highest catalytic activity related to the gas and hydrogen production for the Ni/ZnAl (1:1)-NH_4OH catalyst might be due to the presence of most reducible Ni-based compounds in the catalyst, where Ni metal is known to be effective for hydrogen production from steam reforming of hydrocarbons. Since, as shown in (Fig. 1 (d)), a strong reduction peak was observed around 540 ˚C for the Ni/ZnAl (1:1)-NH_4OH catalyst. The reduction peak around 540 ˚C during the TPR analysis was ascribed to the reduction of surface Ni-Al compounds (likely non-stoichiometric nickel aluminate) and the reduction peak at around 800 ˚C was suggested to be stoichiometric nickel aluminate [14,15]. In addition, the XRD analysis (Fig. 2) confirms the larger presence of NiO crystal phases for the Ni/ZnAl (1:1)-NH_4OH catalyst compared with other catalysts. The presence of $NiAl_2O_4$ and $ZnAl_2O_4$ in the Ni/ZnAl (1:1)-NH_4OH catalyst (Fig. 2 (c)) might also contribute to the highest hydrogen production from gasification experiment.

When the precipitation agent was changed from NH_4OH to Na_2CO_3 for the preparation of the Ni/Ca-Al (1:9) catalyst, hydrogen production and concentration were improved (Table 1). For example, the hydrogen production was increased from 12.7 to 17.8 mmol g^{-1}, and the H_2 concentration was increased from 41.4 to 51.0 Vol.%. The better performance of the Ni/Ca-Al (1:9)-Na_2CO_3 compared with the Ni/Ca-Al (1:9)-NH_4OH was suggested to the availability of

NiO particles observed on the surface of the Ni/Ca-Al (1:9)-Na_2CO_3 catalyst; as shown in Fig. 1 (a), reduction of NiO particles was found around 300 ˚C during the TPR analysis. The higher hydrogen production with the Ni/Ca-Al (1:9) catalyst using Na_2CO_3 as agent might also attribute to the presence of $NiAl_2O_4$ crystal (Fig. 2 (d)) compared with the catalyst using NH_4OH as agent (Fig. 2 (a)). It has to be pointed out that the Ni/Ca-Al (1:9)-Na_2CO_3 presented a higher hydrogen production although it has lower BET surface area (54.7 m^2 g^{-1}), compared with the Ni/Ca-Al (1:9)-NH_4OH with a BET surface area of 79.7 m^2 g^{-1}.

3.2. TPO results of the reacted catalysts

Temperature programmed oxidation (TPO) of the reacted catalysts was carried out to obtain the amount of carbon deposited on the surface of the reacted catalysts. The results are shown in Fig. 3. The mass decrease occurring at around 200 °C was regarded as moisture evaporation; the weight increase around 400 °C was suggested to be the oxidation of the reduced Ni species of the reacted Ni-based catalyst; since the Ni/CaAl and Ni/ZnAl catalysts were reduced during the gasification process where large amounts of reducing agent such as CO and H_2 were present [16].

From Fig. 3, the coke deposition was almost negligible on the surface of the reacted catalysts. However, the reacted Ni/ZnAl (1:9)-NH_4OH has more coke deposition compared with the reacted Ni/ZnAl (1:1)-NH_4OH. It is suggested that the addition of Zn has a positive effect on the prohibition of coke deposition; the higher content of Zn resulted in a lower amount of coke deposition after the gasification process. Furthermore, the preparation agent of Na_2CO_3 for the Ni/CaAl catalyst was observed to exhibit a better performance in relation to the coke deposition compared with the NH_4OH preparation agent, as the coke deposition on the reacted Ni/CaAl (1:9)-Na_2CO_3 is lower than the reacted Ni/Ca-Al (1:9)-NH_4OH catalyst (Fig. 3). Overall, the coke deposition on the reacted catalyst in this work is low with less than 1 wt.% of the weight of catalyst.

3.3. SEM and TEM analysis of the reacted catalysts

The reacted Ni/CaAl and Ni/ZnAl catalysts were analyzed by SEM. Selected SEM micrographs are shown in Fig. 4. From the SEM analysis, carbon deposition was observed on the reacted catalysts, except for the reacted Ni/ZnAl (1:1)-NH_4OH, which was barely deposited with coke. From Fig. 4 (a), filamentous carbons were clearly observed on the surface of the reacted catalyst. The filamentous carbons have been extensively reported during the catalytic gasification process [17]. In addition, it is suggested that Na_2CO_3 agent used for the preparation of the co-precipitated catalyst was more suitable compared with the NH_4OH agent, in relation to the coke deposition on the reacted catalyst after the biomass gasification; this observation is consistent with the TPO results (Fig. 3) where Ni/CaAl (1:9) catalyst prepared by the Na_2CO_3 agent showed lower coke deposition compared with the NH_4OH agent.

Coke deposition on the surface of the reacted catalyst has also been analyzed by TEM (Fig. 5). The results from the TEM analysis further suggest that the Ni/ZnAl (1:1)-NH_4OH has a better performance related to coke deposition. Since, filamentous carbons could not be found on the reacted Ni/ZnAl (1:1)-NH_4OH catalyst. It is further suggested that Zn is an effective metal for Ni-Al catalysts for the prevention of coke from the gasification of biomass.

4. Conclusions

Catalytic steam pyrolysis/gasification of wood sawdust has been investigated in the presence of various nickel-based catalysts. The results showed that the Ni/ZnAl catalyst had a higher hydrogen production (> 23.9 mmol g^{-1}), compared with the Ni/CaAl catalyst (< 17.8 mmol g^{-1}). Zn metal was found to be more effective according to the prevention of coke deposition on the reacted catalyst, compared with the CaAl catalyst. In addition, Na_2CO_3 catalyst preparation agent was found to reduce the coke deposition on the reacted catalyst (TPO, SEM and TEM analysis), compared with the NH_4OH preparation agent.

Acknowledgement

This work was supported by the UK Engineering and Physical Sciences Research Council under EPSRC Grant EP/D053110/1, International Exchange Scheme from the Royal Society (IE110273), and the Early Career Research Scheme from the University of Sydney.

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Table 1: Yields of products and gas concentrations from various experiments.

Catalyst	**Ni/CaAl (1:9)**	**Ni/ZnAl (1:9)**	**Ni/ZnAl (1:1)**	**Ni/CaAl (1:9)**
Preparation Agent	NH_4OH	NH_4OH	NH_4OH	Na_2CO_3
Gas yield(wt.%)	63.5	73.0	75.9	63.9
Residue yield (wt.%)	29.8	30.6	29.7	30.5
Mass balance (wt.%)	100.8	98.1	96.5	96.1
H_2 yield (mmol g^{-1})	12.7	23.9	25.4	17.8
Gas composition (Vol.%)				
CO	24.8	21.7	20.1	18.6
H_2	41.4	55.3	56.3	51.0
CO_2	25.9	21.3	22.2	25.0
CH_4	5.9	1.1	1.1	4.1
C_2-C_4	2.1	0.6	0.3	1.4

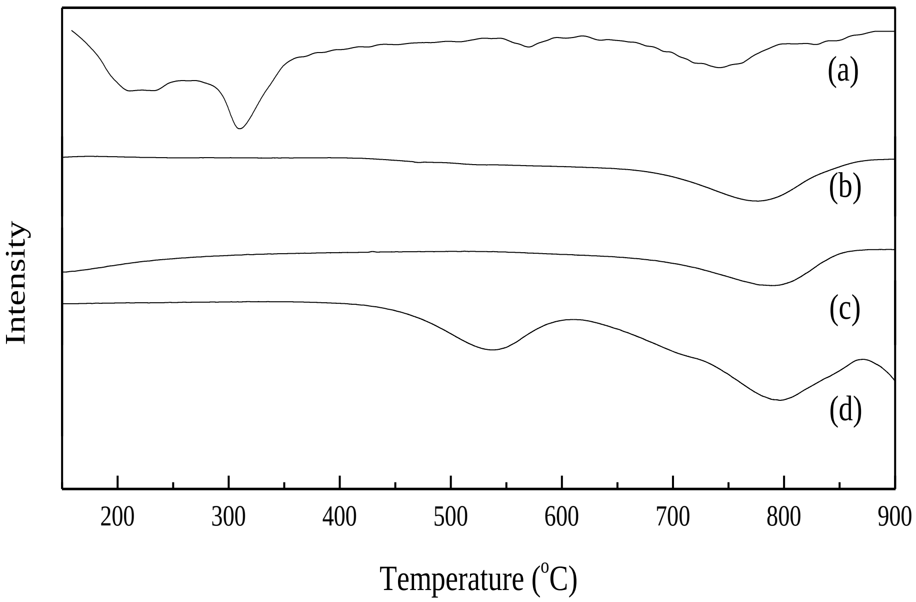


Figure 1. TPR results of the investigated catalysts; (a) Ni/CaAl (1:9)-Na_2CO_3; (b) Ni/ZnAl (1:9)-NH_4OH; (c) Ni/CaAl(1:9)-NH_4OH; (d) Ni/ZnAl (1:1)-NH_4OH

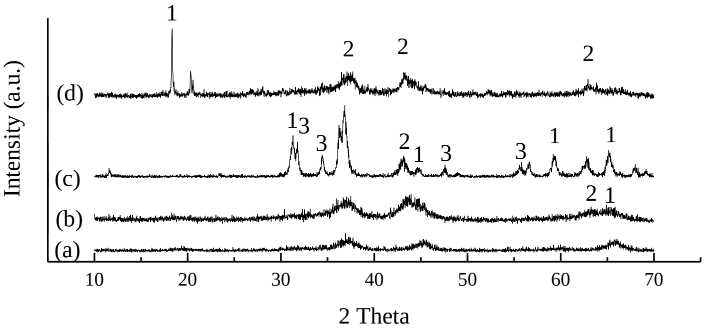


Figure 2. XRD analysis of the fresh catalysts; (a) Ni/CaAl(1:9)-NH_4OH,(b) Ni/CaAl (1:9)-Na_2CO_3, (c) Ni/ZnAl (1:1)-NH_4OH, (d) Ni/ZnAl (1:9)-NH_4OH; 1-$NiAl_2O_4$, 2- NiO, 3-$ZnAl_2O_4$

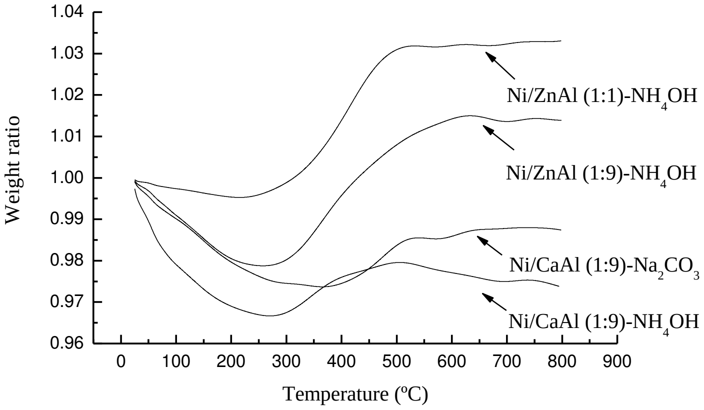
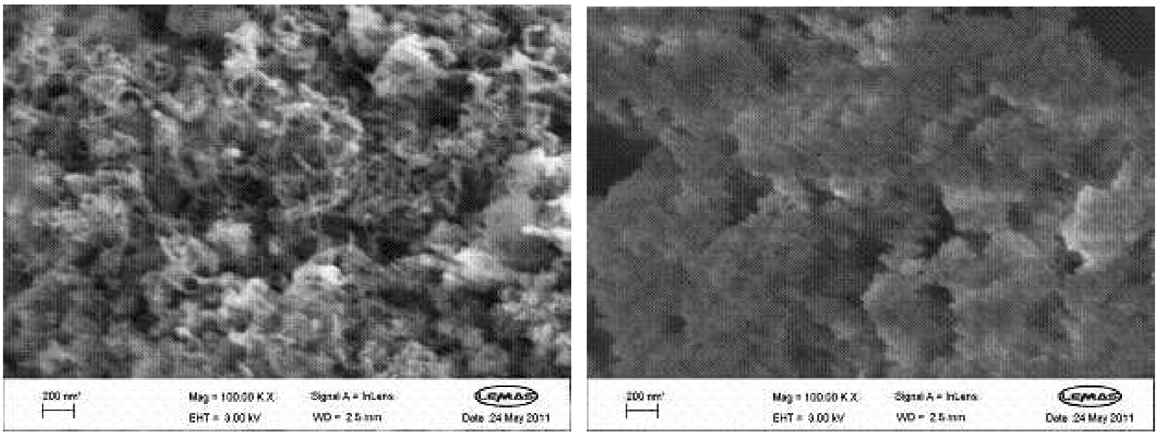
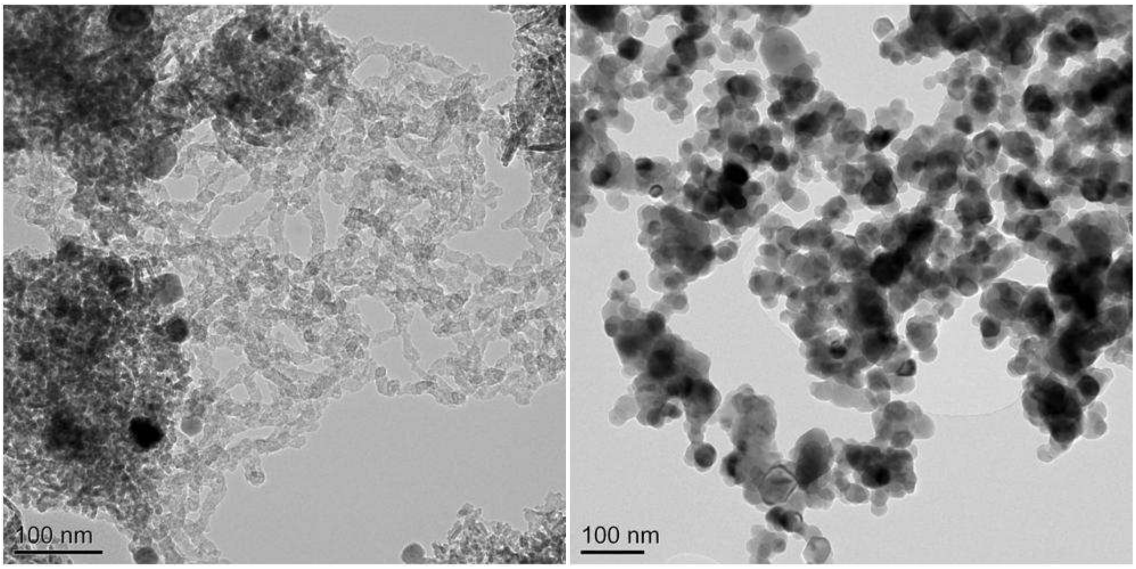


Figure 3: TPO experiments of the reacted catalysts.



(a) (b)

Figure 4: SEM results of the reacted catalyst. (a) Typical SEM picture for the reacted Ni/CaAl (1:9), Ni/ZnAl (1:9) prepared by NH_4OH and Ni/CaAl (1:9) prepared by Na_2CO_3, (b) Reacted Ni/Zn-Al (1:1)-NH_4OH.



(a) (b)

Figure 5: TEM results of the reacted catalyst. (a) Typical SEM picture for the reacted Ni/CaAl (1:9)-Na_2CO_3, Ni/CaAl (1:9)-NH_4OH and Ni/ZnAl (1:9)-NH_4OH (b) Reacted Ni/Zn-Al (1:1)-NH_4OH.