

Investigation of Alumina Supported Mixed Nickel Oxide and Cerium Oxide Catalysts for Syngas Production

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Catalysts containing mixtures of nickel oxide and cerium oxide with different ratio, 1:1, 1:2 and 2:1 were prepared by the sonochemical treatment. The sonication was prolonged for 45 min, constant for each of the catalyst prepared supported by alumina. The resultant catalysts were characterized using X-ray diffraction, scanning electron microscope, energy dispersive X-ray spectroscopy and temperature programmed reduction (TPR) in H₂. The syngas production was detected using temperature programmed gasification and it was done under 5 % oxygen in helium. The coconut shell in powder form (3 μ m) was used as a feedstock. X-ray diffraction patterns shows that all of the catalyst was perfectly matched to the XRD patterns standard of NiO, CeO₂ and alumina, indicating that the catalyst produce through this method were in high purity. Energy dispersive X-ray spectroscopy results further confirmed that all of the elements contain inside the synthesized catalyst were NiO, CeO₂ and alumina were produced in each catalyst. 1:1 ratio of catalyst shows the highest syngas production (H₂/CO) with ratio 0.76 followed by 1:2 and 2:1 with 0.62 and 0.44, respectively. Compared to the standard optimum ratio of syngas which is equal to 1, the experimental value which is 0.76 (nearer to 1), so that it can be used for production of acetic acid and acetyl oxide.

Keywords: Syngas production, Biomass gasification, Mixed nickel oxide, Cerium catalyst.

INTRODUCTION

Biomass is referred as all form of plant material [1]. It is one of the main resources of renewable energy [2]. Gasification of biomass is a thermochemical process [1]. For choosing a suitable feedstock for gasification, it is commonly depends on the feedstock abundance and availability itself [3].

The feedstock that has special attention in this study is coconut shell in the powder form. It is organic in nature and the shell is the most versatile part of the coconut [4]. In Malaysia, huge amount of coconut shell are generated every years, as it is one of the major crops in this country with 142,000 ha of planted land [5].

The catalyst is used in the gasification process purpose to reduce the temperature for devolatilize biomass sample. For example, without the presence of catalyst, the biomass starts to decompose at 270 °C, while in the presence of catalyst the biomass sample has started decomposing at 225 °C [6].

The purpose of this study is to investigate a potential of syngas production from coconut shell in powder form *via* temperature-programmed gasification process using a mixture of NiO and CeO₂ in different ratio as a catalyst. Syngas is

referred as a mixture of carbon monoxide and hydrogen which is converted from the biomass sources and takes place in a gasifier [7].

EXPERIMENTAL

Preparation of biomass: Coconut shells were collected from the area of Kota Bharu. They were then separated by its husk before sun dried. Coconut shells obtained were further grinded into powder form and further sieve (3 μ m) before drying in oven at 338 K for 24 h.

Preparation of mixed nickel oxide and cerium oxide catalysts supported by alumina: Mixture of nickel oxide and cerium oxide catalyst was synthesized by mixing NiO (from Hmbg) and CeO₂ (from Merck) in distilled water (100 mL). Mass of NiO and CeO₂ in each catalyst was different based on their ratio.

Ultrasound irradiation was accomplished with a high intensity ultrasound probe (2 cm diameter Ti-horn, 20 kHz, 500 W) immersed directly in the reaction solution for 45 min. The colour of the solid solution was grey and the resultant grey solid (mixture of NiO and CeO₂) was then recovered using centrifuge technique and subsequently washed sparingly with

distilled water and acetone, then oven dried for overnight at 373 K.

The synthesized mixture of nickel oxide and cerium oxide were then added with α -phase of alumina as a supporter, in distilled water (100 mL). Then, it was stirred on a hot plate for 1 h by using magnetic stirrer.

The solid was again recovered by centrifuge technique, subsequently washed sparingly with distilled water and acetone then oven dried for overnight at 373 K, yielding a homogeneous catalyst.

Catalysts characterization: X-ray diffractogram (XRD) analysis was carried out by using a Shimadzu diffractometer model XRD 6000.

The LEO 1455 variable pressure scanning electron microscope (SEM) was used to observe the morphology of the catalysts. The accelerating voltage applied was 20 kV. The BALTEC 005 sputter coater was used to cover the sample with a thin layer of gold. The SEM images were display as a result of secondary and backscattered electron images were produced as they were generated by the electron beam irradiation and collected by the detector.

Energy dispersive X-ray spectrometer (EDX) was used to determine the elements present in the catalysts. The EDX system is attached to SEM.

H₂-temperature programmed reduction analysis was performed using Thermo Finnigan TPDRO 1100 Series.

Catalysts evaluation: Temperature programmed gasification (TPG) was carried out by using Thermo Finnigan TPDRO 1100 apparatus online with a mass spectrometer (model Quadstar) that able to detect the output gas composition. The coconut shell gasification was done at temperature range from 50 to 900 °C, with a heating rate 10 °C min⁻¹. The temperature was hold for 1 h at final temperature.

The gases that were detected by mass spectrometer were H_2 , CO, CO₂ and CH₄ by following its m/z 2, 28, 44 and 16, respectively. The ratio by mass of catalyst to coconut shell studied was 1:3.

RESULTS AND DISCUSSION

X-ray diffractogram (XRD): The XRD patterns of the catalysts were shown in Fig. 1. All of the catalysts exhibit the characteristics peaks of crystalline CeO₂ (at 2 θ angle of 28.8°, 33.4°, 47.8°, 56.7°, 59.4°, 69.8°, 77.0° and 79.4°), NiO (at 2 θ angle of 63.1°) and Al₂O₃ (at 2 θ angle of 37.6° and 43.5°).

Although the ratio of the NiO and CeO_2 mixed are different, but the produce catalyst did not cause any changes in terms of the basic matrix of NiO, CeO_2 and supporter Al_2O_3 . Therefore, the catalysts produce by sonicating process consist of high purity. This can be further proved that, there are no other impurity crystalline phases are detected in all catalyst samples.

Besides, the size of crystallite was also estimated by the XRD result using Scherrer equation [8],

$$L = K\lambda/\beta.\cos\theta \tag{1}$$

where L = average crystallite size, K = constant which is normally taken as 0.9, λ = X-ray wavelength, β = peak width of the diffraction peak profile at half maximum height and α can be either in degrees or radians.

Fig. 1. XRD patterns of mixed metal oxide catalyst with different ratio

The crystallite size of 1:1, 1:2 and 2:1 mixture of NiO/ CeO₂ catalyst are 33.10, 36.88 and 40.32 nm, in average respectively (Table-1). When the amount of nickel increases as shown in 2:1 catalyst, the crystallite size of catalyst also increase. The larger the size of catalyst is, the smaller the surface area will be. Furthermore, the smaller surface area will also decrease the active site of the catalyst. This decreasing active site will decrease the contact frequency between the catalyst and coconut shell [11]. This is in agreement with the obtained data in the syngas production.

TABLE-1			
AVERAGE OF CRYSTALLITE SIZE FROM XRD RESULT (nm)			
Catalyst	Average of crystallite size (nm)		
1:1	33.10		
1:2	36.88		
2:1	40.32		

Scanning electron microscope (SEM): The surface morphologies of the mixed nickel oxide and cerium oxide catalysts synthesized by sonication method were examined using scanning electron microscope with 5000 magnification as shown in Fig. 2.

All of the catalyst shows their plate-like structure without symmetry staggered to each other. The particles are also shown in agglomerate form. Energy dispersive X-ray spectroscopy were used to further confirm all of the elements presence in the catalyst synthesized.

Energy dispersive X-ray spectroscopy (EDX): The elements content in the catalyst were confirmed using EDX. All of the elements were presence in 1:1, 1:2 and 2:1 mixture of NiO/CeO₂ catalyst as shown in Table-2.

For 1:1 mixture of NiO/CeO₂ catalyst, the mean for Ni, Ce and Al contains were 23.59, 25.80 and 6.35 %, respectively (Table-2). While, for 1:2 mixture of NiO/CeO₂ catalyst, it contain 18.41 % Ni, 25.08 % Ce and 10.47 % Al as shown in Table-2. The 2:1 mixture of NiO/CeO₂ catalyst, as analyzed by EDX, were containing 20.76 % Ni, 15.46 % Ce and 19.17 % Al (Table-2). Hence, it is confirmed that all of the elements were present in each sample.







Fig. 2. SEM micrographs of mixed metal oxide catalyst with different ratio (a) 1:1 (b) 1:2 (c) 2:1 (with 5000× magnification)

TABLE-2 AVERAGE OF ELEMENTS CONTENT IN MIXED METAL OXIDE CATALYST WITH DIFFERENT RATIO (%)					
Catalyst	С	0	Al	Ni	Ce
1:1	14.84	29.42	6.35	23.59	25.80
1:2	19.91	26.15	10.47	18.41	25.08
2:1	11.39	33.21	19.17	20.76	15.46

Temperature programmed reduction (TPR in H₂/Ar): The reduction profiles of 1:1, 1:2 and 2:1 mixture of NiO/CeO₂ catalysts were shown in Fig. 3. There was a maximum peak exhibited by each catalyst. The rate of hydrogen consumption was at 422, 400 and 416 °C for 1:1, 1:2 and 2:1, respectively. The amount of oxygen removed by the reaction with H₂ for this 1:1, 1:2 and 2:1 mixture of NiO/CeO₂ catalyst were 0.36, 0.17 and 0.62×10^{22} atoms g⁻¹, respectively (Table-3).



Fig. 3. Temperature programmed reduction profiles for the 1:1, 1:2 and 2:1 of mixed metal oxide catalyst

TABLE-3 TOTAL AMOUNT OF OXYGEN REMOVED FROM MIXED METAL OXIDE CATALYST WITH DIFFERENT RATIO			
Catalyst T _{max} (K)		Oxygen atom removed ($\times 10^3$ mol g ⁻¹)	Oxygen atom removed $(\times 10^{22} \text{ atoms g}^{-1})$
1:1	695	5.9	0.36
1:2	673	2.8	0.17
2:1	689	10.3	0.62

The hydrogen consumption of 1:2 mixture of NiO/CeO₂ catalyst was the lowest with 0.17×10^{22} atoms g⁻¹. It is known that, CeO₂ units are very mobile and leave the ceria lattice easily [9], so the oxygen released from this process should be high as the cerium oxide content is highest if compared to the other samples studied. However, in this study, the oxygen released is the lowest. This is due to the CeO₂ reduction hidden because its external surface is significantly lowered by the presence of Ni [10]. It suggest that the Ni presence was cover up the surface of CeO₂. Therefore, it is not possible for CeO₂ to release its oxygen.

Temperature programmed gasification (TPG): The highest ratio of syngas production (H₂/CO) was 1:1 mixture of NiO/CeO₂ catalyst with 0.76, contributed by the high hydrogen produce, 0.8282 cm^3 (Table-4). The highest hydrogen produce was due to its smallest particle size which is 33.10 nm, estimated by XRD result as shown in Table-1.

TABLE-4 SYNGAS AND BYPRODUCT PRODUCE (cm ³) BY MIXED METAL OXIDE CATALYST WITH DIFFERENT RATIO					
Catalyst	H_2	CO	CO_2	CH_4	H ₂ /CO
1:1	0.8282	1.0882	3.0199	1.6895	0.76
1:2	0.7816	1.2539	2.0907	1.4915	0.62
2:1	0.5968	1.3580	3.0164	1.9997	0.44

The smaller the size of catalyst is, the higher the surface area will be. Furthermore, the high surface area will also increase the active site of the catalyst. This increasing active site will increase the contact frequency between the catalyst and coconut shell [11]. Hence, hydrogen production becomes increase.

While, 2:1 mixture of NiO/CeO₂ catalyst produces the lowest ratio of syngas production (H₂/CO) with 0.44 and this is due to the lowest hydrogen production, 0.5968 cm³, if compared to other catalysts. The higher particle size will lower the surface area and reduce the active site of the catalyst synthesized contribute to the lower hydrogen production.

Furthermore, the lower hydrogen production is also due to the CH_4 in 2:1 mixture of NiO/CeO₂ catalyst does not broken down into H₂. This clearly shown in Table-4 that CH_4 produce by 2:1 mixture of NiO/CeO₂ catalyst was the highest with 1.9997 cm³ if compared to the other catalyst studied.

The total of CO and CO_2 produced by the 2:1 mixture NiO/CeO₂ catalyst was the highest with 1.3580 cm³ and 3.0164

cm³ respectively if compared to 1:1 and 1:2 mixtures of NiO/ CeO₂ catalysts (Table-4).

Based on the CO production, it is suggested that the nickel content in the catalyst promote partial oxidation as in 2:1 catalyst. Furthermore, the oxygen being removed from the catalysts was also contributed to the CO and CO₂ produced. The more oxygen was removed from the catalyst, the higher tendency of the oxygen to react with carbon and produce CO and CO₂ (reaction 2 and 3 [12]). This is in agreement with the result obtained from temperature programmed reduction in H₂ (Table-3).

$$C + \frac{1}{2}O_2 \longrightarrow CO \tag{2}$$

$$C + O_2 \longrightarrow CO_2 \tag{3}$$

Conclusion

The gasification of coconut shell was carried out by using 1:1, 1:2 and 2:1 ratio of mixed NiO/CeO₂ catalyst and coconut shell in powder form (catalyst: biomass = 1:3) at temperature 50 to 900 °C and hold for 1 h at the end temperature. 1:1 mixed NiO/CeO₂ catalyst produce the highest syngas (H₂/CO) ratio, 0.76 due to its smaller crystallite size, higher surface area and high contact frequency between the catalyst and coconut shell. While, 2:1 mixed NiO/CeO₂ catalyst produce high CO content and this shows nickel promote the partial oxidation. The result also shows that the coconut shell can be gasified using mixed NiO/CeO₂ catalyst with ratio catalyst: coconut shell = 1:3 at temperature range 50-900 °C.

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