THE EFFECTS OF DIFFERENT SONICATION TIMES OF NICKEL OXIDE AND ZIRCONIUM OXIDE CATALYSTS IN SYNGAS PRODUCTION

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Graphical abstract

Catalyst Synthesis

Two different Metal oxides (NiO and ZrO₂) at ratio 1:1 + distilled water

Expose to ultrasound irradiation (30, 60 and 90 mins)

Zeolite supporter (Impregnation method)

Calcine at 500 °C for 4 h

Catalyst Characterization

(XRD, TPR-H₂, BET, SEM, TEM)
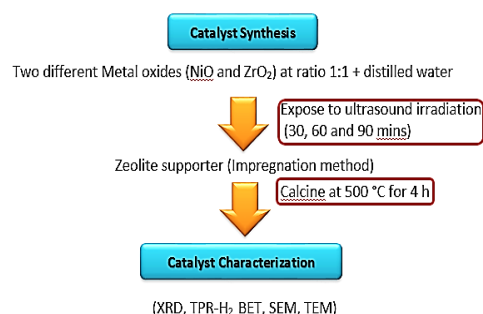
Abstract

Heterogeneous catalytic cracking is currently one of the most effective ways for both reducing tar content and enhancing hydrogen (H_2) content in syngas at relatively low temperature, besides being environmental friendly. Sonochemical treatment has also been shown to lower reaction times with enhanced reaction rate and enables production of particles with high surface area. In this study, two different types of metal oxides, which are Nickel oxide (NiO) and Zirconium oxide (ZrO_2) at a combination of 1:1 ratio with Zeolite as the supporter are synthesized via sonochemical treatment in durations of 30, 60 and 90 minutes. The catalysts are then characterized using X-Ray Diffraction (XRD), Temperature Programmed Reduction (TPR-H_2), Brunauer-Emmett-Teller surface measurement (BET), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). From SEM and TEM analysis, Nickel tends to agglomerate and form sizable globular shapes, Zirconium forms coral-like branching structure and Zeolite forms stacks of cubic clumps. The most promising sonication treatment duration for the catalysts is 30 minutes because it removes decent amount of reactive oxygen at a rate of 0.83×10^{21} atoms/g during hydrogen reduction, possesses the highest surface area of 506.52 m^2/g as well as smallest average crystallite size of 56.9 nm compared to other durations. Generally sonochemical treatment also increases the catalysts surface area and oxygen removal as well as lowers the reduction temperature which is favourable in term of production cost. Catalysts with sonochemical treatment duration of 30 and 60 minutes generally show higher reactive oxygen removal and surface area compared to catalysts with 90 minute treatments.

Keywords: Heterogeneous catalysts, nickel oxide, zirconium oxide, biomass, gasification

Abstrak

Retakan pemangkin heterogen kini merupakan salah satu cara yang paling berkesan untuk mengurangkan kandungan tar dan meningkatkan kandungan hidrogen (H_2) dalam syngas pada suhu yang agak rendah, selain mesra alam sekitar. Rawatan Sonokimia juga telah menunjukkan pengurangan masa reaksi dengan kadar tindak balas yang lebih baik dan membolehkan pengeluaran zarah dengan luas permukaan yang tinggi. Dalam kajian ini, terdapat dua jenis oksida logam iaitu Nikel oksida (NiO) dan Zirkonium oksida (ZrO_2) dengan kombinasi nisbah 1: 1 dengan Zeolite sebagai penyokong disintesis melalui rawatan sonokimia dalam tempoh 30, 60 dan 90 minit. Mangkin yang dihasilkan kemudiannya dicirikan dengan menggunakan X-Ray Diffraction (XRD), Reduced Programmed Temperature (TPR-H_2), Pengukuran luas permukaan Brunauer-Emmett-Teller (BET), Mikroskopi Pengimbasan Elektron (SEM) dan Transmisi Elektron Mikroskopi (TEM). Dari analisis SEM dan TEM, nikel cenderung menggumpal dan membentuk bentuk globular yang cukup besar, Zirkonium membentuk struktur cabang seperti karang dan bentuk zeolit membentuk rumpuk padu. Tempoh rawatan sonikasi yang paling menjanjikan untuk pemangkin adalah 30 minit kerana ia menghilangkan jumlah oksigen reaktif yang baik pada kadar 0.83×10^{21} atom / g semasa pengurangan hidrogen, mempunyai luas permukaan tertinggi 506.52 m2 / g serta purata kristal terkecil saiz 56.9 nm berbanding tempoh rawatan yang lain. Rawatan sonokimia secara amnya juga meningkatkan luas permukaan pemangkin dan penyingkiran oksigen serta mengurangkan suhu pengurangan yang menguntungkan dari segi kos pengeluaran. Pemangkin dengan tempoh rawatan sonochemical 30 dan 60 minit secara amnya menunjukkan penyingkiran oksigen reaktif yang lebih tinggi dan kawasan permukaan berbanding pemangkin dengan rawatan 90 minit.

Kata kunci: Pemangkin heterogen, nikel oksida, zirkonium oksida, biomas; gasification

1.0 INTRODUCTION

The depletion of world petroleum reserves and increased environmental concerns has stimulated the search for the alternative renewable fuels that are capable of fulfilling an increasing energy demand. The biomass fuels represent an abundantly available and renewable energy resource with CO_2 neutral impact. It is the only sustainable source of energy and organic carbon for industrial society [1]. Among different processes for their utilization, the biomass gasification is one of the best options in order to optimize the conversion of the chemical energy of the fuel. Instead of using edible biomass (sugars, starches, and vegetable oils) for large scale production of fuels, the development of nonedible biomass (lignocellulosic biomass) permits sustainable and cheaper production of fuels and chemicals without affecting food supplies [1]. Biomass gasification is one of the most promising options for converting lignocellulosic biomass to synthesis gas (syngas), a mixture of CO and H_2, which can be used either as a fuel to produce heat and power or as an intermediate in the production of liquid fuels (e.g. diesel fuel, dimethyl ether) and chemicals (e.g. methanol).

Tar is a complex mixture of condensable organic compounds, which includes single ring to 5-ring aromatic compounds along with other oxygen-containing hydrocarbons and complex polycyclic aromatic hydrocarbons (PAHs), which can foul the equipment and cover the surface of catalysts to slow or stop the reaction [2]. Tars present a number of process challenges, including coking of catalysts and condensation on downstream piping, filters, and other equipments. The tar removal cost is as expensive as the overall process to produce syngas [3].

Tars cause severe operational problems associated with their condensation and polymerization. Tar removal is a critical issue in the development of biomass gasification, especially in the Fischer–Tropsch (F–T) synthesis where those impurities can lower the F-T activity in the bio-syngas catalytic conversion [2], . Moreover, a high H_2/CO ratio in the gas stream is desirable for F-T synthesis.

Catalytic cracking/ reforming is currently one of the most effective ways for both reducing tar content and enhancing H_2 content in syngas at relatively low temperature. Recently, conventional homogeneous based catalysts are expected to be replaced in the near future by environmentally friendly heterogeneous based catalysts mainly because of environmental constraints and simplifications in the existing processes. Heterogeneous catalytic is considered as a

technology with the highest potential to contribute to the solution of tar decomposition. In addition, the use of a catalyst can enhance the gas yield and promote the reforming reactions of residual hydrocarbons. In heterogeneous reaction, the interaction of methane with metals results in H_2 evolution where at temperature above 400 K, dehydrogenation of CH_x species becomes fast and the elemental carbon is more stable forming stronger bonds with the metal surface [4].

Several catalytic materials have been studied as additives in fluidized-bed reactor in order to achieve in situ catalytic conditioning of the product gas inside the gasifier reactor. Many works on in-bed catalysts consider dolomite [2, 5, 6], olivine [3, 6], nickel [2, 3, 5-8] and noble metal (NM) based catalysts [4]. A tar conversion rate of 99 % has been achieved by using dolomite and Ni-based catalysts [2]. The catalytic performance of dolomite in tar cracking is directly proportional to the number of surface base sites [3].

Although NMs, such as Ru, Rh, Pd, Pt, and Ir, have been studied extensively for dry reforming reaction, their high cost and limited availability limits their industrial applications [9]. Nickel-based catalyst has been considered as the most suitable due to its fast turnover rates, long-term stability and lower cost [4]. However, the major challenge in many processes involving Ni-based catalyst is deactivation by carbon deposition [2]. Therefore, an effective catalyst that minimizes coke deposition should be developed. Zirconium has been tested as a base catalyst to reform gas containing tarry impurities. Zirconium catalyst works efficiently in decomposing tars, especially heavier hydrocarbons. In several tests done by Simell and Kurkela [10], zirconium catalysts provided a tar conversion of 60 to 80 % at a temperature of about 600 ^{0}C. Zirconium has also been used as support for Ni-based catalyst for syngas production by dry reforming reaction, which enables direct conversion of natural gas into liquid fuels at remote extraction sites [4].

Metal oxides are constituents of the Earth crust and have been catalyzing different important reactions in chemical evolution. They are good adsorbents and efficient catalysts [11]. They consist of dispersed surface metal oxide species and catalytic active sites supported on high surface area oxides [12]. Mixed metal oxide catalysts are used in heterogeneous catalysis for chemical processes and being further developed for their catalytic performance and durability [13]. Supported metal oxide catalysts have been extensively investigated since 1950s. According to Lee and Wachs [14], the surface metal oxide species of supported metal oxide catalysts control the overall catalytic performance such as activity and selectivity. Zirconium oxide (ZrO_2) has high thermal stability as a catalyst support. It is proven to be a very good promoter for cobalt catalyst where it enhanced CO conversion rate and C5+ selectivity [2]. A study comparing Ni/CeO_2, Ni/ZrO_2, and Ni/CeO_2-ZrO_2 mixed oxide catalysts for methane partial oxidation

at 700 °C showed higher activity and coke resistance on the composite supports as compared to the individual metal oxides [6]. Another study using combination of Ni-Ce-ZrO_2 catalyst showed high conversions of reactants (97%) and provide high resistance to catalyst deactivation, but still requires a high temperature [4].

Catalytic performances are expected to be improved by the optimization of the catalytic filter system and the use of more active in-bed catalysts. In this study, the catalysts used are two different types of metal oxides, which are Nickel Oxide (NiO) and Zirconium Oxide (ZrO_2) with Zeolite supporter. Zeolites have been added to the conventional F-T system in many studies. They have a shape-selective property that restrains the formation of products that are larger than the size of the zeolite channels and result in lighter hydrocarbons. Zeolites acid site can help with cracking, isomerization and aromatization reactions for F-T products [2]. They are also widely used in heterogeneous catalysis because of their well-defined pore structures and capabilities of extremely high surface area and surface acidity [6].

The catalysts used for this study were synthesized via sonochemical treatment. Sonochemically assisted reactions showed lower reaction times with enhanced reaction rate. It enables production of small and high uniform particles sizes with high surface area, metal dispersion and defects that have been shown to play a crucial role in catalysis [15-20]. The utilization of sonochemical treatment in the synthesis of the catalysts was proven to show significant increase in the catalytic activity, stability and selectivity of catalysts [20].

2.0 METHODOLOGY

2.1 Preparation of Mixed Nickel Oxide and Zirconium Oxide Catalysts

Mixture of NiO and ZrO_2 catalysts was synthesized by co-precipitation method by mixing NiO (from Hmbg) and ZrO_2 (from Acros Organics) based on NiO to ZrO_2 ratio of 1:1 in 100 mL distilled water. The solutions were then sonicated at different durations, which were 30, 60, and 90 minutes with 2 cm diameter Ti-horn, 20 kHz, 500 W probe. The temperature was kept constant at 80 °C. A separate mixture of NiO and ZrO_2 with the same ratio but without sonication treatment was also prepared. The samples were then cooled to room temperature. The resultant solid (mixture of NiO and ZrO_2) was then recovered using centrifuge for 5 minutes at 2000 rpm [21]. It was then subsequently washed with distilled water followed by washing with acetone to remove the by-products [22] before oven dried overnight at 105 °C for 12 hours according to Tao *et al.* [23].

2.2 Preparation of Zeolite NaY Supporter

The supporter used was Zeolite Y sodium (Zeolite NaY), procured from Alfa Aesar. Table 1 shows the mole ratio and surface area.

Table 1 Mole ratio and surface area of Zeolite NaY

Zeolite NaY characterization	SiO_2	Al_2O_3
Mole ratio	5.1	1
Surface area (m²/g)		900

Zeolite NaY was first treated with sonochemical treatment for 60 minutes and the resultant solid was

Table 2 Denotations of prepared catalysts

Sonochemical treatment duration (min)	NiO:ZrO₂ ratio 1:1 catalyst denotation
0	1:1:00
30	1:1:30
60	1:1:60
90	1:1:90

2.3 Catalyst Characterization

The catalysts are then characterized through a series of analysis as follows. X-ray diffraction (XRD) analysis is carried out using Shimadzu diffractometer model XRD 6000. Hydrogen temperature programmed reduction analysis (H_2-TPR) is performed using Thermo Fisher Scientific TPDRO 1100 apparatus that is equipped with a thermal conductivity detector (TCD). The total surface areas of the catalysts are then measured using Thermo Electron Sorptomatic 1990 and Quantachrome AS1Win™ Automated Gas Sorption Data Acquisition and Reduction utilizing Brunauer-Emmett-Teller (BET) method. Electron microscopy technique is used to obtain the information on the morphology and size of the catalyst samples by using LEO 1455 Variable Pressure scanning electron microscope (SEM). The particle size of the samples are examined using Hitachi H-7100 energy filter transmission electron microscope (TEM).

3.0 RESULTS AND DISCUSSION

3.1 X-Ray Diffraction (XRD) Analysis

X'Pert HighScore software from PANalytical B. V. was used to analyze the XRD data. From the XRD data of all samples, the presence of NiO phase appeared consistently at 2θ = 37.3°, 43.4°, 62.8° and 75.4° (JCPDS File No. 00-022-1189) but the peak intensities are very low. This might be due to high metal dispersion of NiO on the surface of Zeolite NaY. The presence of ZrO_2 phase appeared at multiple degrees = 24.0°, 24.3°,

recovered using centrifuge before oven dried overnight at 105 °C. The synthesized mixture of NiO and ZrO_2 were then added with Zeolite at a loading of 10 g equally, in 100 mL distilled water. The mixture was then stirred on a hot plate with a magnetic stirrer for one hour. The solid was again recovered using centrifuge technique and subsequently washed with distilled water followed with acetone then oven dried overnight at 105 °C for 12 hours [23]. The catalysts mixtures were then calcined in air at 500 °C for 4 hours, yielding a homogeneous catalyst powder, according to Klimova *et al.* [24] and Maciel *et al.* [25]. Calcining the synthesized catalysts powders also removes structure directing agents and other organic substances present in them [26]. The prepared catalyst samples denotations are as shown in Table 2. 28.4°, 31.7°, 34.4°, 35.6°, 40.9°, 49.4°, 50.3°, 50.8°, 54.2°, 55.5°, 58.6° and 62.2° (JCPDS File No. 00-013-0307). While Zeolite NaY showed multiple peaks at 2θ = 6.4°, 10.5°, 12.2°, 15.9°, 19.0°, 20.6°, 23.0°, 24.0°, 27.3°, 29.9°, 31.1°, 31.7°, 34.4°, 40.9°, 49.4° and 54.2° (JCPDS File No. 00-038-0239). Some of the peaks of ZrO_2 and Zeolite NaY seem to overlap with each other and it is quite difficult to distinguish the peaks between the two.

Based from the peak intensities of the sonochemically treated catalysts with NiO:ZrO₂ ratio of 1:1 as shown in Figure 1, they generally show a trend of peaks with higher intensities as the treatment duration increases from 30 to 90 minutes. However there is no significant difference between the untreated catalysts with the 60 and 90 min treated ones. This indicates that sonochemical treatment does not have significant effects on the structures and crystallinity of the catalysts after 60 and 90 minutes, except for the first 30 minutes where the peak intensities are significantly reduced by 22.8 % especially for ZrO_2 and Zeolite NaY phases.

Zeolite NaY generally has the highest crystallinity and more defined structure compared to NiO and ZrO_2. The size of crystallite can be estimated from the XRD data as shown in Table 4, using Scherrer equation [27],

$$L = K\lambda/\beta.\cos\theta \qquad (1)$$

where L = average crystallite size, K = constant which is normally taken as 0.9, λ = X-ray wavelength, β = peak width of the diffraction profile at half maximum height and θ can be either in degrees or radians.
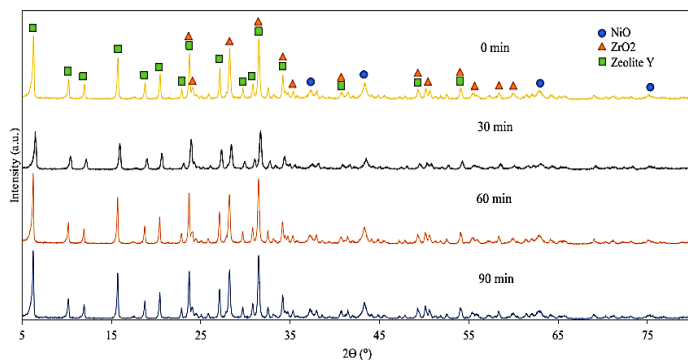
Figure 1 XRD patterns of NiO:ZrO$_2$ catalysts ratio 1:1 treated with sonochemical treatment for 0, 30, 60 and 90 minutes

3.2 Temperature Programmed Reduction (TPR in H$_2$/Ar)

All catalyst samples produced a single reduction peak at temperature ranging from 637 K to 709 K as shown in Figure 2 and Table 3.
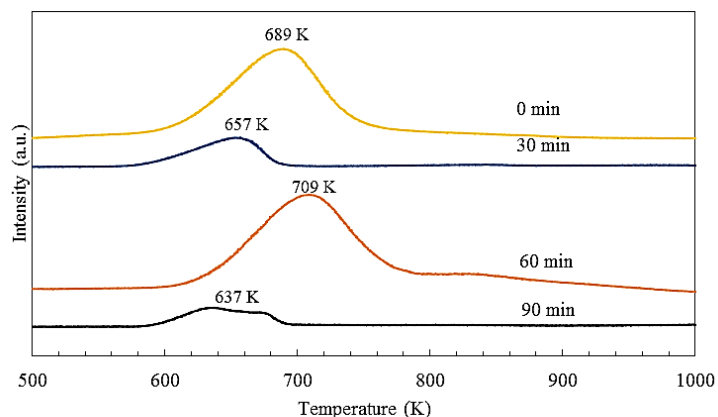

Figure 2 Temperature programmed reduction profiles for NiO:ZrO$_2$ ratio 1:1 with different sonication times

Table 3 Total amount of oxygen removed from the catalysts by reduction in H$_2$/Ar

Catalyst	T_{max} (K)	H$_2$ gas adsorbed (x10^{-3} mol/g)	Total O$_2$ removed (x10^{21} atoms/g)
1:1:00	689	6.69	4.03
1:1:30	657	1.37	0.83
1:1:60	709	7.81	4.70
1:1:90	637	0.99	0.60

As can be seen in Table 3, catalyst with sonochemical treatment duration of 60 minutes removed the highest amount of oxygen at 4.70 x10^{21} atoms/g. However, shorter and longer treatment duration significantly decreased the amount of oxygen removed. From the data, it is shown that catalyst with sonochemical treatment duration of 60 minutes is the most efficient reactive oxygen removal while catalyst sonochemically treated for 90 minutes is the least efficient with reactive oxygen removal at 0.60 x10^{21} atoms/g. This might be due to the agglomeration of NiO and ZrO$_2$ has reduced the dispersion of the active metal phases on Zeolite NaY support and consequently causing less contact between the reactants and the active sites. However, production cost-wise, catalyst sample 1:1:30 and 1:1:90 have lower T_{max} at 657 K and 637 K respectively compared to catalyst sample 1:1:00 and 1:1:60. Despite the much lower reactive oxygen removal rate from catalyst sample 1:1:30, it has much lower T_{max}, which also indicates that it has faster reaction at lower temperature, thus can be considered to be cost-efficient in large biomass gasification industry.

3.3 Scanning Electron Microscopy (SEM)

In all samples, NiO tends to agglomerate into large globular shape while Zeolite NaY forms stacks of cubic shaped clumps and mostly spread out throughout the entire samples. ZrO$_2$ is the smallest particle among the other two catalysts. It was seen to be in cylindrical form in coral-like branching structure distributed throughout the sample. Figure 3, 4 and 5 show large globular clumps of NiO surrounded by Zeolite NaY and some smaller coral-like ZrO$_2$ clumps can be seen around it.

The longer the sonication treatment duration, the more agglomerated the catalysts become and the size of NiO globular clumps tends to grow bigger as Ni agglomerates.
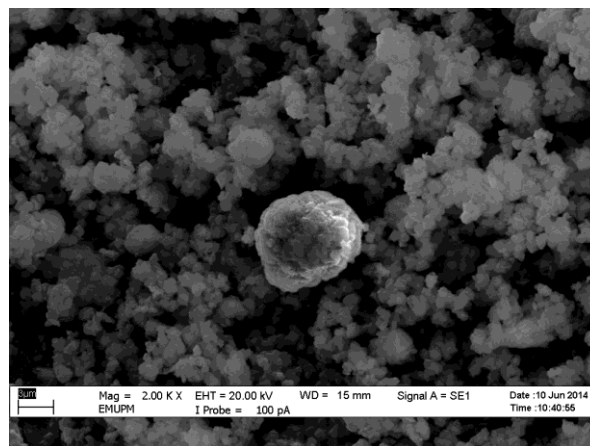

Figure 3 SEM micrograph of catalyst sample 1:1:30 at magnification 2000 x
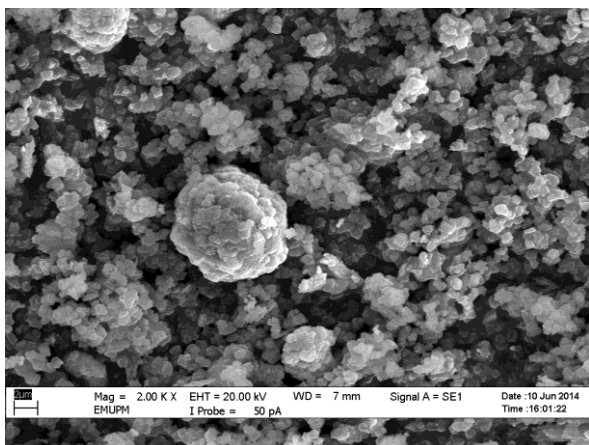
Figure 4 SEM micrograph of catalyst sample 1:1:60 at magnification 2000 x
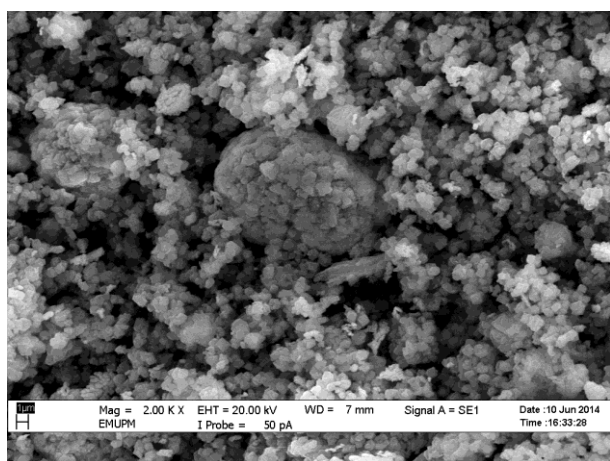

Figure 5 SEM micrograph of catalyst sample 1:1:90 at magnification 2000 x

3.4 Transmission Electron Microscopy (TEM)

Figure 6 shows agglomerated NiO particles with sizes ranging from 6 to 12 nm in sample 1:1:30. Also from the same sample, ZrO_2 forms coral-like branching structures with diameters ranging from 74 to 95 nm as shown in Figure 7. While crystal-like Zeolite NaY stacks up on each other with diameters ranging from 201 to 493 nm as can be seen in Figure 8.
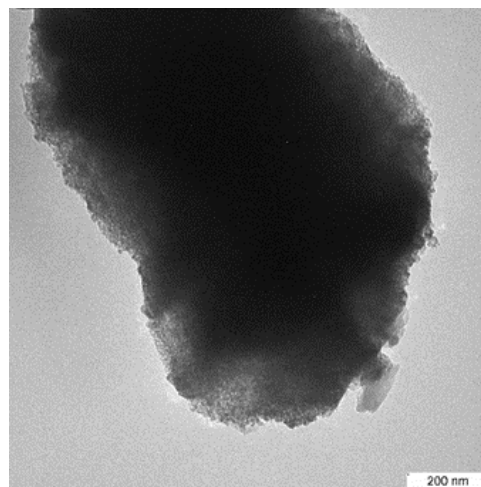

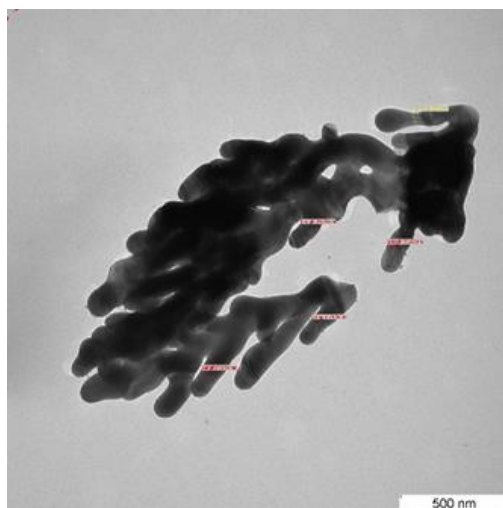**Figure 6** TEM micrograph of NiO in catalyst sample 1:1:30 at magnification 100 000 x

Figure 7 TEM micrograph of ZrO_2 in catalyst sample 1:1:30 at magnification 50 000 x
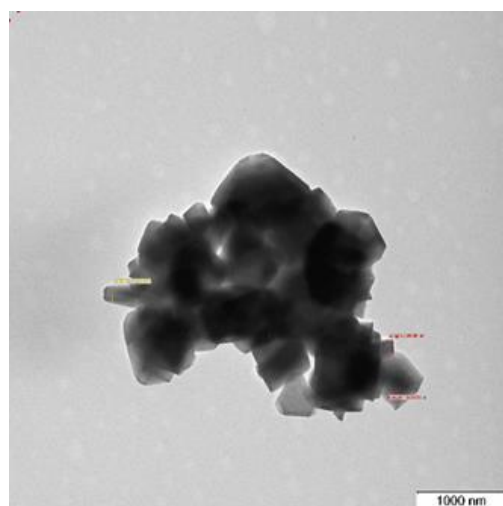

Figure 8 TEM micrograph of Zeolite NaY in catalyst sample 1:1:30 at magnification 20 000 x

Table 4 Particle size of catalyst sample 1:1:30

Catalyst	Min (nm)	Max (nm)	Average (nm)	Standard deviation (σ)
NiO	6.2	11.9	7.8	1.9
ZrO_2	74.3	95.1	86.9	7.2
Zeolite NaY	201.4	492.9	306.7	108.4

3.5 BET Surface Area Measurement

Based from Table 5, catalyst with the highest surface area is sample 1:1:30 with surface area of 506.52 m^2/g and the lowest surface area is catalyst sample 1:1:90 with surface area of 472.58 m^2/g. This is in agreement with the XRD data where sample 1:1:30 also has the smallest average crystallite size of 56.9 nm compared to catalyst sample 1:1:60 and 1:1:90. The presence of Zeolite NaY supporter and ZrO_2 in catalysts was reported by Derekaya and Yasar [28] to give higher surface area compared to catalysts without their presence. Zeolite NaY also has high surface area (900 m^2/g) and well dispersed pore structure. ZrO_2 was also implied to act as a surface area agent.

However there is a huge discrepancy between pure Zeolite NaY surface area (900 m^2/g) and treated Zeolite NaY surface area. The drying and calcination of catalysts could also possibly affect the total surface area. This also means that both NiO and ZrO_2 loading on Zeolite NaY significantly reduced the surface area of Zeolite NaY. Also it is shown that the longer the duration of sonication treatment, the lower the surface area of the catalyst. This might be due to further agglomeration of active metal Ni on the surface of Zeolite NaY where it could lead to blockage of pores and reduction to the overall surface area of Zeolite NaY [17].

Table 5 Specific BET surface area of NiO:ZrO_2 catalysts

Catalyst	Surface area (m^2/g)
1:1:00	476.36
1:1:30	506.52
1:1:60	475.00
1:1:90	472.58

4.0 CONCLUSION

The catalysts studied, which are NiO and ZrO_2 with Zeolite NaY supporter will help in the study of catalytic cracking and reforming mechanisms in good quality and cleaner syngas production. However the results are not conclusive yet since syngas evaluation using Temperature Programmed Gasification (TPG) has not been done yet. The results from TPG analysis will determine the performance of the catalysts and will relate with the catalysts characterization data. For now, it can be said the most promising sonication treatment duration for NiO:ZrO_2 catalyst ratio 1:1 is 30 minutes because it produces the smallest average crystallite size, removes reactive oxygen at a decent rate and produces the highest surface area. These are properties of good catalysts. Generally sonochemical treatment also increases the catalysts surface area and oxygen removal as well as lowers the reduction temperature which is favourable in term of production cost. Extended exposure to sonochemical treatment beyond 60 minutes caused the catalysts particles to be highly agglomerated especially for NiO and reduced its active phase dispersion on the surface of Zeolite NaY support which then negatively affect the catalysts' effectiveness in removing reactive oxygen. From SEM and TEM analysis, NiO tends to agglomerate and form sizable globular shapes, ZrO_2 forms coral-like branching structure and Zeolite NaY forms stacks of cubic clumps. From the catalysts characterization data and analysis obtained, catalyst with NiO:ZrO_2 ratio of 1:1 and 30 minutes of sonochemical treatment seems to be a promising catalyst for producing rich syngas with higher catalytic activity and reaction.

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