

THE EFFECT OF NiO LOADS ON CATALYTIC ACTIVITY OF NiO/ZSM-5 FOR TRANSESTERIFICATION OF RUBBER SEED OIL

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ABSTRACT

In this investigation, a series of NiO/ZSM-5 with different NiO loads were produced and applied to catalyze transesterification of rubber seed oil (RSO) with methanol. ZSM-5 was prepared using hydrothermal technique from rice husk silica (RHS) and Al(OH)₃ without using a template and then impregnated with Ni(NO₃)₂ solution of different concentrations followed by 6 hr calcination at 600 °C. Characterizations were performed with Fourier transform infrared (FTIR) spectroscopy, x-ray diffraction (XRD), scanning electron microscope (SEM), and x-ray fluorescence (XRF). The establishment of ZSM-5 was confirmed by XRD and SEM, and NiO/ZSM-5 by XRD, SEM, and XRF. Catalytic activity tests demonstrate a significant enhancement of performance of NiO/ZSM-5 compared to that of ZSM-5 without NiO. Practically complete conversion of RSO into methyl esters was achieved with the use of NiO/ZSM-5 catalysts prepared using 5, 10, and 15% nickel solution; however, decreases with the use of 20% nickel solution. In this respect, it can be concluded that a 5% nickel solution is sufficient to produce NiO/ZSM-5 enabling complete conversion of RSO into biodiesel, suggesting that NiO/ZSM-5 is a prospective heterogeneous catalyst for biodiesel production.

Keywords: Rubber Seed Oil, Biodiesel, Heterogeneous Catalyst, NiO/ZSM-5

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INTRODUCTION

With respect to current renewable energy development, biodiesel has particular importance since it has been commercially produced and used as a fuel in blend with petrochemical diesel. Apart from this successful utilization, biodiesel is still more expensive than petrochemical diesel due to higher production costs, primarily contributed by raw material and processing. Feedstock remains the main contributor to the production cost since, up to the present, the biodiesel industry still relies on coconut oil and palm oil. These two edible vegetable oils (EVOs) have been known for a long time as functional oil used not only in food industries but also for the production of various oleochemicals. With such wide utilization, not only the price of these oils is relatively high, but their use for energy should also be limited for food security considerations.

In an attempt to reduce the production cost of biodiesel, the initiative currently undertaken is an exploration of non-edible vegetable oils (non-EVOs). In addition to a significant reduction of cost, elimination of competition with the food industry is another advantage offered by non-EVO. Concerning these advantageous features, the utilization of many types of non-EVO has been explored. Several examples are *Jatropha curcas* oil^{1,2}, *Ricinus communis* oil^{3,4}, yellow oleander seed oil⁵, pine oil⁶, *Calophyllum inophyllum* L⁷, and sunflower oil.^{8,9} Another prospective raw material is rubber seed oil (RSO), particularly in many tropical regions, including Indonesia, where rubber plantation is an important agriculture sector. In addition to high availability, another characteristic that makes rubber seed an attractive resource is its appreciable oil content, which is in the range of 38 to 50% mass.^{10,11}

Production of biodiesel is a catalytic reaction in which vegetable oil (VO) is reacted with simple alcohols, most commonly methanol. In this reaction, free fatty acids and glycerides composing the oil are converted into fatty acid methyl esters (FAMES) through esterification and transesterification, respectively. Vegetable oil and alcohol are not reactive to each other, and therefore the use of catalysts is necessary.

Traditionally, homogeneous catalysts are used, either strong mineral acids such as phosphoric acid¹² and sulfuric acid or strong alkaline such as NaOH^{6,13} and KOH.^{7,14} While high yield is generally achieved with homogeneous catalysts; their use is not without some drawbacks; most obviously is difficult to remove the catalyst from biodiesel and the corrosive nature of the homogeneous catalyst.

Due to the disadvantageous of a homogeneous catalyst, the development of heterogeneous catalysts is rapidly growing. Non-toxicity and simplicity to separate biodiesel and catalyst are the main advantages offered by a heterogeneous catalyst. Besides, reuse of heterogeneous catalysts is highly possible. The most widely used heterogeneous catalyst is a composite catalyst, in which metal oxide is supported onto porous solids include silica, alumina, and zeolite. Using silica as a solid support, various heterogeneous catalysts have been developed with different metal oxides as an active site, such as CaO¹⁵, MgO¹⁶, TiO₂.¹⁷ Several metal oxides such as CaO and K₂O have also been supported on alumina.^{18,19} Another type of solid support that has been reported is zeolite and has been used for different oxides and metals such a CaO²⁰, MgO²¹, Ni, Co, and Mo.²²

The utilization of zeolite as solid support is interesting since zeolite itself already has catalytic activity, and different types of zeolite have been used as a catalyst to produce biodiesel from several feedstocks, such as waste cooking oil²³, maggot oil²⁴, and sunflower oil.⁹ In this regard, the metal oxide loaded on zeolite is expected to enhance the performance of the catalyst.

In this study, ZSM-5 zeolite prepared from RHS and aluminum hydroxide was impregnated with nickel nitrate solution with different concentrations to produce NiO/ZSM-5 with different NiO loads. The produced composites were then tested as catalysts for the transesterification of RSO with CH₃OH, with the main purpose to examine the influence of NiO loads on the performance of NiO/ZSM-5 as a catalyst.

EXPERIMENTAL

Material and Instruments

RHS and RSO used were laboratory stocks from previous studies.¹¹ The chemicals used are reagent grade Al(OH)₃, CH₃OH, HNO₃, NaOH, NH₄NO₃, and Ni(NO₃)₂.6H₂O. Instruments used are electrical furnace (Nabertherm, Lilienthal, Germany), Fourier transforms infra-red (FTIR) spectrometer Cary 630 model, gas chromatography-mass spectrophotometer (GC-MS QP 2010S SHIMADZU), SEM Carl Zeiss/Evo MA 10, XRD PANanalytical type Epsilon, and the XRF PANanalytical type Epsilon 3.

General Procedure

Preparation of ZSM-5

For the preparation of ZSM-5, a mass of 6.6 g of NaOH pellet was dissolved in distilled water (120 mL). An aliquot of 100 mL of the NaOH solution was used to dissolve 30 g RHS, and the rest 20 mL was used to dissolve 1.95 g of aluminum hydroxide. The two solutions were transferred into a polypropylene chamber followed by addition of distilled water (100 mL), and then slowly agitated for 3 hr with a magnetic stirrer. The mixture was aged at ambient temperature for 24 hr in a Teflon-lined autoclave. The crystallization process was carried out for 48 hr at 180 °C by placing the autoclave in an oven. After the crystallization process was completed, the solid product was washed using distilled water until the filtrate had a neutral condition, and subsequently oven-dried for 8 hr at 110 °C. Finally, the sample was ground into 200 mesh powder and calcined at 600 °C for 6 hr.

Preparation of NiO/ZSM-5

A mass of 5 g ZSM-5 was transferred into 50 mL of Ni(NO₃)₂.6H₂O solution, magnetically stirred for 6 hr after that allowed for 24 hr at ambient temperature. The mixture was filtered and the solid was slowly rinsed with 100 mL distilled water three times, and then oven-dried for 12 hr at 100 °C. Finally, the solid was subjected to a calcination process at 550 °C for 6 hr.²⁵ The NiO/ZSM-5 with different loads of NiO were prepared by using the solution of Ni(NO₃)₂.6H₂O with varying concentrations of 5, 10, 15, and 20%.

Characterization

FTIR spectra were collected adopting the technique of KBr pellet on a Cary 630 infrared spectrophotometer in the range of wavenumber at 4000-500 cm⁻¹. Characterization with x-ray was carried out with the

instrument operated at 40 mA current, 40 kV energy, and Cu K α radiation. Diffractogram was recorded at 2θ from 5–60° and with an increase of 2°/min. The micrographs were recorded using Carl Zeiss/Evo MA 10, operated with 15 kV energy with the window wide (WD 9.0 mm). XRF analysis was carried out using PANalytical Epsilon 3 operated at a maximum voltage of 50 kV, current 1 mA, and power 9 W.

Catalytic Activity Test

For the activity test, a 500 mL round bottom flask containing a reaction mixture composed of RSO (10 mL), methanol (60 mL), and catalyst (1 gram) was situated on a heating mantle, and a reflux condenser with water cooling was assembled on the flask. The reaction was run at 70 °C for 3 hr, left to cool, and finally poured into a separating funnel. The biodiesel layer was separated from unreacted methanol and oil. The biodiesel volume was measured for the determination of oil conversion. GC-MS analysis was carried out, followed by identification of the components using database Library System NIST62, Wiley 7.

RESULTS AND DISCUSSION

FTIR Characterization

The FTIR spectrum of ZSM-5 and that of one of NiO/ZSM-5 samples as a representative are shown in Fig.-1.

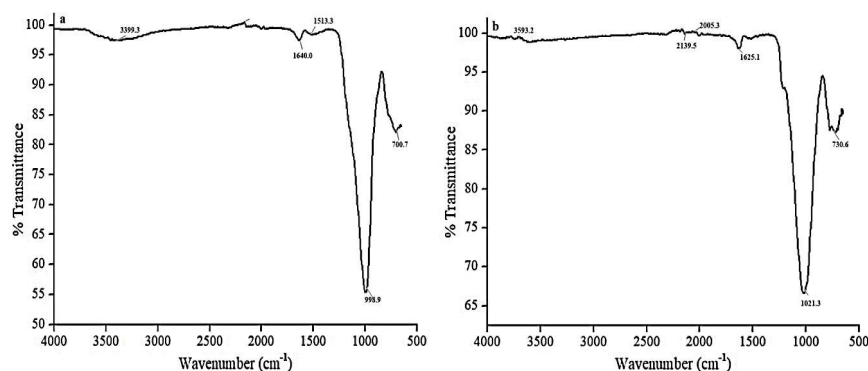


Fig.-1: (a) FTIR Spectrum of ZSM-5 and (b) FTIR Spectrum of NiO/ZSM-5

The two spectra are practically similar, marked by a band at around 1000 cm^{-1} as the main band. This band is a characteristic band of zeolite resulting from the vibration of Si-O-Al and Si-O-Si groups. The band also justifies the presence of these two functional groups at 700-730 cm^{-1} . The bands at about 3400 cm^{-1} and 1625-1640 cm^{-1} are resulted from the vibration of -OH functional group in silanol and adsorbed water molecules.²⁶

XRD Characterization

The XRD diffractogram of the sample is presented in Fig.-2, indicating the existence of crystalline phases in the samples, which implies that silica and alumina have reacted under the experimental conditions applied.

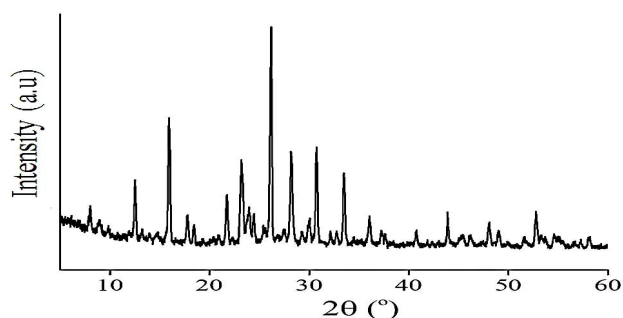


Fig.-2: XRD Diffractogram of Synthesized ZSM-5

To confirm the existence of ZSM-5, the XRD pattern of the sample was compared with the pattern of standard published in the International Zeolite Association (IZA) database, and the results are shown in Table-1.

Table-1: XRD Data of the ZSM-5 Synthesized and the Data of IZA ZSM-5 Standard

IZA ZSM-5 Standard		ZSM-5 Synthesized	
2 θ	Relative Intensity (%)	2 θ	Relative Intensity (%)
7.94	100	7.94 ₍₉₅₎	44.62
7.96	57.17	7.96 ₍₆₂₎	45.72
8.02	26.45	8.02 ₍₀₀₎	13.89
8.80	35.52	8.86 ₍₈₆₎	35.37
23.03	15.92	23.03 ₍₉₈₎	44.30
23.08	36.52	23.08 ₍₉₉₎	59.90
23.24	14.09	23.24 ₍₀₃₎	42.45
23.10	25.36	23.19 ₍₀₂₎	100
23.20	5.98	23.27 ₍₃₇₎	84.72

The results in Table-1 confirmed the formation of the ZSM-5 as indicated by the characteristic peaks of ZSM-5 listed in the IZA database, although significantly different intensities should be acknowledged. The most significant difference is the position of the peak with the highest relative intensity (100%), in which for ZSM-5 standard, the peak is located at $2\theta = 7.94^\circ$ while for the sample investigated is located at $2\theta = 23.19^\circ$. This difference in the peak position with the highest intensity is most likely due to the use of a template for the preparation of ZSM-5 standard, while in this present study, no template was used. The results obtained in this study, the location of the peak with the highest intensity, in particular, are in agreement with findings by others who also synthesized ZSM-5 without the use of a template.^{27,28}

SEM Characterization

Fig.-3 displays the micrographs for ZSM-5 and that of NiO/ZSM-5 resulting from impregnation with 10% nickel solution.

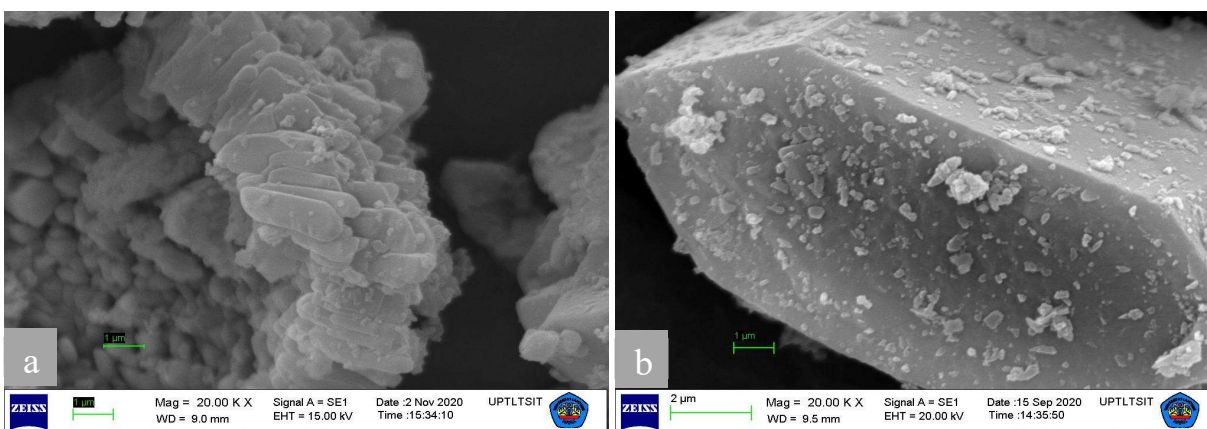


Fig.-3: (a) SEM Micrograph of ZSM-5 and (b) SEM Micrograph of NiO/ZSM-5

As can be seen, the existence of crystalline ZSM-5 is quite evident in the form of hexagonal, which is a characteristic shape of ZSM-5 particle^{27,28}, although the existence of an amorphous state should also be mentioned. From the results of XRD and SEM characterization, it can be seen that the formation of ZSM-5 is supported by these two characterization methods. Another piece of information in Fig.-3 is that impregnation of ZSM-5 causes no significant change in the shape of the particle.

XRF Analysis

The XRF results showing the NiO content of the ZSM-5 samples impregnated with nickel solution of different concentrations are presented in Table-2, indicating that impregnation has taken place and succeeded in inserting Ni²⁺ ions into zeolite framework and through calcination, the ions were converted into NiO.

Table-2: NiO Content of NiO/ZSM-5 Prepared Using Nickel Solution with Different Concentrations

The Concentration of Nickel Solution (%)	NiO Content of NiO/ZSM-5 (%)
0	0.004
5	1.255
10	2.081
15	2.126
20	0.239

As can be seen in Table- 2, the ZSM-5 without impregnation was found to contain a small quantity of NiO (0.004%) in an unimpregnated sample is most likely due to measurement error. The results also display that NiO content of the samples increases with increased concentration of nickel solution up to 15%, and then decreases with the use of nickel solution with a concentration of 20%. This decrease implies that optimum absorption of Ni²⁺ ions was achieved with the use of nickel solution with a concentration of 15%, and for the more concentrated solution, the surface of the zeolite was likely has become saturated and led to more prominent desorption than adsorption of Ni²⁺.

Transesterification Experiments

Effect of NiO Loads on the Percent of Conversion of RSO

To evaluate the effect of NiO contents, the five NiO/ZSM-5 samples were applied as a catalyst in the transesterification of RSO, producing the data in Table- 3.

Table-3: Percent of Conversion of RSO Using NiO/ZSM-5 with Different NiO Contents

NiO Content of NiO/ZSM-5 (%)	% Conversion of RSO
0.004	60
1.255	≈100
2.081	≈100
2.126	≈100
0.239	70

The experiment data demonstrated the significant ability of NiO in promoting the catalytic performance of the NiO/ZSM-5. Three catalysts with NiO contents of 1.255, 2.081, and 2.126%, respectively, were found to give complete conversion of RSO. In this respect, it can be implied that NiO content of 1.255% is sufficient to optimize the catalytic performance of NiO/ZSM-5.

Analysis of Transesterification Products

The transesterification of RSO with methanol is a conversion of the fatty acids into FAMES. To confirm the formation FAMES, the product of the transesterification experiment using NiO/ZSM-5 with NiO content of 1.255% was analyzed with GC-MS. The GC chromatogram of the sample analyzed is shown in Fig.- 4.

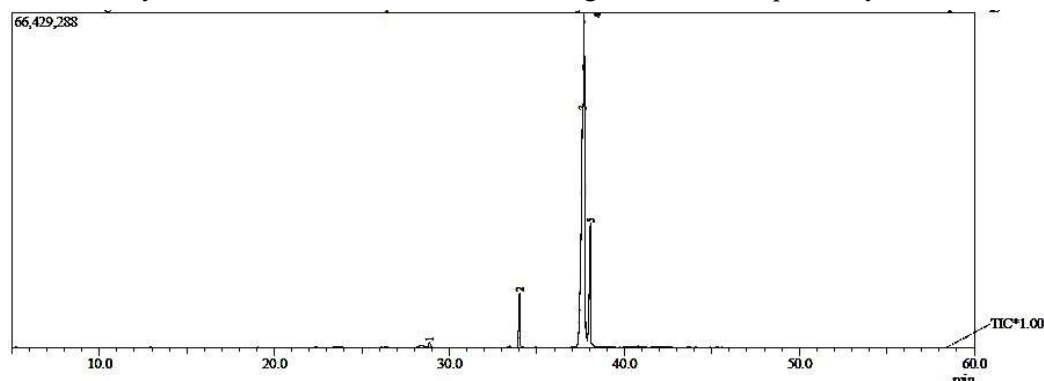


Fig.-4: GC Chromatogram of Transesterification Result of RSO Using NiO/ZSM-5 with NiO Content of 1.255% as a Catalyst

Table-4: Chemical Composition of Transesterification Product of RSO Using NiO/ZSM-5 with NiO Content of 1.255% as a Catalyst

Peak No	Retention Time (min)	Compound Name	Relative Percentage
1	22.5	Methyl laurate	0.22
2	34.05	Methyl myristate	6.27
3	37.52	Methyl palmitate	25.45
4	37.64	Methyl stearate	54.02
5	38.08	Methyl oleate	14.89
6	41.56	Methyl linoleate	0.14

Table-4 shows the chemical composition of the product derived from the transesterification of RSO with methanol. As can be observed, the sample components are fatty acid methyl esters, and no other type of compound was detected, thus confirming that the fatty acids in RSO are completely converted into biodiesel. Also, the distribution of the components is in agreement with fatty acids contained in RSO, as reported by previous workers.^{11,29}

CONCLUSION

The results obtained demonstrate that ZSM-5 zeolite can be produced from RHS and aluminium hydroxide without using a template, and the zeolite can be doped with NiO by the impregnation method. Characterization using XRD and SEM justified of ZSM-5 and formation of NiO/ZSM-5 was confirmed using XRF measurement. Catalytic activity assay reveals that the introduction of NiO results in significant enhancement of catalyst performance, and complete conversion of RSO into biodiesel was achieved using the catalyst with NiO content of 1.255%. In this respect, it is concluded that NiO/ZSM-5 is a very prospective heterogeneous catalyst for biodiesel production.

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