EFFECT OF THERMAL TREATMENT AND NICKEL-SALT MODIFICATION ON THE CATALYTIC PERFORMANCE OF THE ILLITE-KAOLINITE CLAY FROM BUKITTINGGI OF WEST SUMATRA IN PALM OIL TRANSESTERIFICATION

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Abstract

The effect of thermal and chemical modification on the catalytic performance of illite-kaolinite clay (obtained from Bukittinggi, West Sumatra) in the transesterification of palm oil was investigated. Characterization with XRD, XRF and FTIR indicated a slight change in the composition of the crystal phase and the Si/Al molar ratio after such clay was calcined at 450 °C. XRF measurements also confirm that after treatment with two nickel salts, the natural clay absorbs more nickel sulfate than nitrate, while temperature played an important role in increasing the performance of the clay in loading nickel about 2 times bigger at a higher temperature. All clay-based materials prepared in this study were tested for their catalytic activity and selectivity in the transesterification of palm oil to produce Fatty Acid Methyl Ester (FAME) using the previously reported procedure. Chemical modification of clay samples with nickel sulfate and nickel nitrate was found to increase the catalytic performance of the clay in producing FAME from 38 to about 60 % while thermally treated at 450 °C yielded slightly higher to about 67 %. In terms of selectivity, all clay-based catalysts in this study gave almost the same amount of saturated and unsaturated FAME

Keywords

Introduction. Currently, depleting fossil fuel reserves and environmental problems such as emission of pollutants and greenhouse gases are complex problems that can only be solved by using alternative energy [1]. Especially for the problem of decreasing diesel oil reserves, now it can be overcome slowly by mixing or replacing the fuel with what is known as biodiesel. It has been reported that the use of biodiesel provides an environmentally friendly concept because its use can reduce pollution due to smog, acid rain, carbon monoxide emissions, unburned hydrocarbons, polycyclic aromatic hydrocarbons, and particulates, and can also reduce the greenhouse effect [2].

Biodiesel feedstock is very abundant because it comes from animal and vegetable oils. Vegetable oils commonly used are palm oil, soybeans, and jatropha. Indonesia has the potential to convert palm oil into biodiesel because around 85–90 % of the world's Crude Palm Oil (CPO) production comes from Indonesia and Malaysia [3]. Generally, bbiodiesel was produced by catalytic transesterification and esterification reaction. Homogeneous catalysts are still commonly used because of their high catalytic activity, but there are some problems such as the difficulty of separation and purification process, they cannot be reused, even worst is corrosion of equipment due to the large amount of wastewater generated [4]. So heterogeneous catalysts are better used because of their advantages in relatively lower production costs, not easy to rust, non-toxic, not having parallel reactions such as saponification, biodiesel produced with high purity, easy separation and purification, and comparable catalyst activity with homogeneous catalysts [5, 6].

The heterogeneous catalyst prepared in this work is clay because it is abundant and easy to obtain in all regions of Indonesia. Based on data from the Ministry of Energy and Mineral Resources of the Republic of Indonesia, clay is the second largest material after limestone owned by this country. Several studies have been conducted to apply natural clays as catalysts and catalyst supports for biodiesel production from palm oil such as clays obtained from Sawahlunto and Indarung (West Sumatra) which are enriched with Ca and Cu [7], and another approach in which clay obtained from Padang (West Sumatra) is composited with graphene oxide [8]. Based on these studies, the catalytic properties of clay are determined by the specific surface area, pore diameter and the type of metal being loaded which requires chemical or physical modification to improve its catalytic properties and activity.

Nickel is known to be a good catalyst in biomass conversion [9], by adding some amount of nickel onto calcined chicken eggshell catalyst confirmed that biodiesel production yield can be obtained up to 100 % [10], but there is still few study on the incorporation of nickel salts with clay as a catalyst in the

transesterification reaction to produce biodiesel. In this report, we present thermal treatment and modifications with nickel nitrate and nickel sulfate of kaolinite-illite based clay obtained from Bukittinggi (West Sumatra) and then compare the effect of these modifications on the catalytic activity of these clays in the transesterification of palm oil to produce methyl esters. Furthermore, by combining the two nickel salts with clay, the toxicity of the two nickel salts that will be used in this study can be overcome because there is an easy procedure to separate them from the reaction products.

Experimental. *Material.* The clay was obtained from one of the locations in the Bukittinggi area (West Sumatra). Methanol 98 % (Merck) is used as a source of methyl groups in the transesterification reaction of crude palm oil as a raw material to produce Fatty Acid Methyl Ester (FAME). Two nickel salts $Ni(NO_3)_2 \cdot 6H_2O$ 99 % (Merck) and $NiSO_4 \cdot 6H_2O$ 99 % (Merck) were used as nickel sources. Aquadest is used to prepare a solution of the two nickel salts.

Characterization methods. XRD (*Xpert Pro PANalytical PW30/40*) equipment was run to characterize the mineral composition while XRF (*Epsilon 3* Spectrometer) measurements were to determine the elemental composition of the clay sample. FTIR (*Shimadzu, IR Tracer-100 AH*) was used to analyze the presence of organic groups remaining after the calcination process of clay samples and GC-MS (*Shimadzu QP 2010 SE*) to determine quantitatively and qualitatively the FAME produced from the catalyzed palm oil transesterification reaction.

Thermal and chemical treatment. Thermal treatment for clay samples was carried out as follows: Firstly the clay samples was cleaned by soaking it in distilled water for 24 hours and filtered. The clay was then resuspended in distilled water and continued by centrifugation for 15 minutes at 3000 rpm and the solid obtained was dried at 105 °C for 4 hours. Then the clay sample that has been treated was sieved through a 90 μm sieve and named as heated-clay (h-clay). The h-clay sample was calcined at a temperature of 450 °C for 4 hours, followed by grinding and sieving with a 90 μm sieve. The sample was named calcined-clay (c-clay). The mineral and elemental compositions of h-clay and c-clay were characterized by XRD and XRF while the presence of organic and inorganic functional groups were analyzed by FTIR.

The following procedure was performed to chemically modify clay samples; Some h-clay was reacted with 0.5 M $NiSO_4$ solution (mass ratio of h-Clay: $NiSO_4$ volume = 1 : 10), stirred for 24 hours at room temperature at 500 rpm then was named h-clay/NS29 and the one prepared at 70 °C was named h-clay/NS70. The obtained catalyst materials were rinsed with distilled water until the color of the filtrate was no longer green and was dried then at 105 °C for 4 hours.

The same process was carried out for nickel nitrate which was incorporated to the clay using a 0.5 M $Ni(NO_3)_2$ solution, the samples were then named h-clay/NN29 for the reaction at 29 °C and h-clay/NN70 for the reaction at 70 °C. The amount of nickel loaded by h-clay and c-clay of the two types of nickel salts at room temperature and at 70 °C were measured by XRF.

Transesterification reaction. The clay-catalyzed palm oil transesterification reaction was carried out according to the previously reported [4, 8] procedure through a reflux process with the following steps; the reaction was conditioned in which the mole ratio of CPO-methanol was 1 : 6 and the volume-to-mass ratio of methanol-catalyst was 10 : 1. First, the catalyst and methanol are reacted with continuous stirring until 50 °C. Then 50 mL of dried palm oil was put into a three-neck flask. The reflux process was continued for another 4 hours at 85 °C and stirred at 700 rpm. After the reaction is complete, the flask is cooled to room temperature. The catalyst is separated from the product mixture using filter paper. The reaction product was then washed with hot water (50 °C) with a volume ratio of 1 : 1 and homogenized for 5 minutes until a whitish-yellow liquid was formed. The mixture is left for about 12 hours to allow the product to separate from the water in the bottom layer. The product obtained was separated by filter paper to remove glycerol. The biodiesel obtained was heated at 105 °C until no more bubbles were seen. Products suspected of containing methyl esters were analyzed by GC-MS and methyl ester obtained from the transesterification of palm oil calculated based on equation [5]:

$$\text{Yield (\%)} = \frac{\text{Mass of methyl esters } x \text{ \% FAME from GC-MS}}{\text{Mass of CPO}} \cdot 100 \text{ \%}.$$

Result and discussion. *Effect of thermal treatment.* XRF measurements were carried out to determine the elemental composition contained in claysamples heated at 105 °C (h-clay) and calcined at 450 °C (c-clay). As can be seen in Table 1, that the Bukittinggi clay is composed of about 70 % silicon and aluminum elements. The other dominant element is iron (about 20 %) and is accompanied by minor elements such as calcium, titanium, potassium and sodium.

Table 1

Comparison of the elemental composition of h-clay and c-clay measured with XRF

Element	Samples before and after calcination, %	
	h-clay	c-clay
Si	48.5	49.4

End of the Table 1

Element	Samples before and after calcination, %	
	h-clay	c-clay
Al	23.0	23.6
Fe	19.6	18.2
Ca	3.83	3.71
Ti	1.95	1.83
Na	1.48	1.68
K	1.25	1.21
Mg	0.34	0.37
Ni	0	

Thermal treatment by means the calcination process of the clay has caused the color to change from brown to red. The calcination process did not have a significant effect on the Si/Al mole ratio of the clay, which only slightly changed from 2.00 to 2.01. The calcination process in this case is more aimed at removing organic components and opening the pores so that it can enlarge the specific surface of the clay. Theoretically, the larger the specific surface area of a heterogeneous catalyst, the higher its catalytic activity [11].

X-ray diffraction is useful for studying the types of minerals present in clay. From the XRD diffractogram (Fig. 1), it can be seen that the Bukittinggi clay is composed of illite and kaolinite (a typical clay mineral) with albite as other
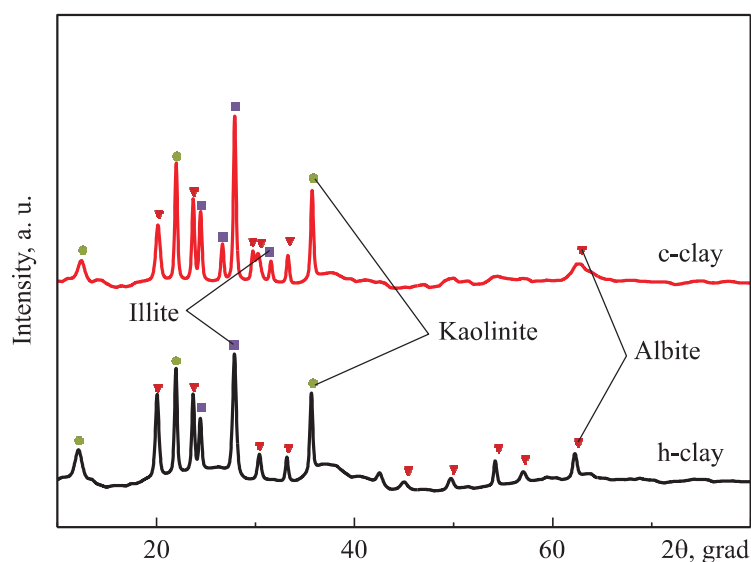

Fig. 1. Comparison of the mineral composition of h-clay and c-clay measured with XRD

minerals. The diffraction pattern with the highest peak of 2θ at 28° is illite (ICDD No. 00-002-0050) and 2θ at 22° for kaolinite (ICDD No. 00-001-0527) and 2θ at 24° which is albite (ICDD No. 01-083-1606). What we can observe is that the calcination process at a temperature of 450 °C is an increase in the amount of kaolinite minerals followed by a decrease in the amount of illite minerals with a slight decrease in illite peaks at 28 and 32°. But in general the calcination process only slightly changes the clay mineral composition where the illite and kaolinite peaks tend to remain stable followed by the loss of a number of albite as non-clay minerals. In the catalytic process, the structural resistance of these clay minerals will have a good influence because they are the minerals that provide the catalytic effect or in other ways become an important part in supporting its performance as a catalyst support [12, 13].

The effect of calcination on chemical bonding in clay was investigated by FTIR instrument and it shown in Fig. 2. It can be seen that compared to h-clay, for all infrared absorption patterns of c-clay slightly shifted towards a larger wavenumber except for the strain band OH. This kind of shift indicates a small dealumination in the clay mineral structure due to weaker Al–O bonds than Si–O and causes Si–O vibrations to become more dominant [14]. The adsorption at 3632 and 1634 cm^{-1} respectively indicated the presence of O–H stretching bands and H–O–H bending of kaolinite where this absorption was weakened in c-clay due to the reduction in the number of water
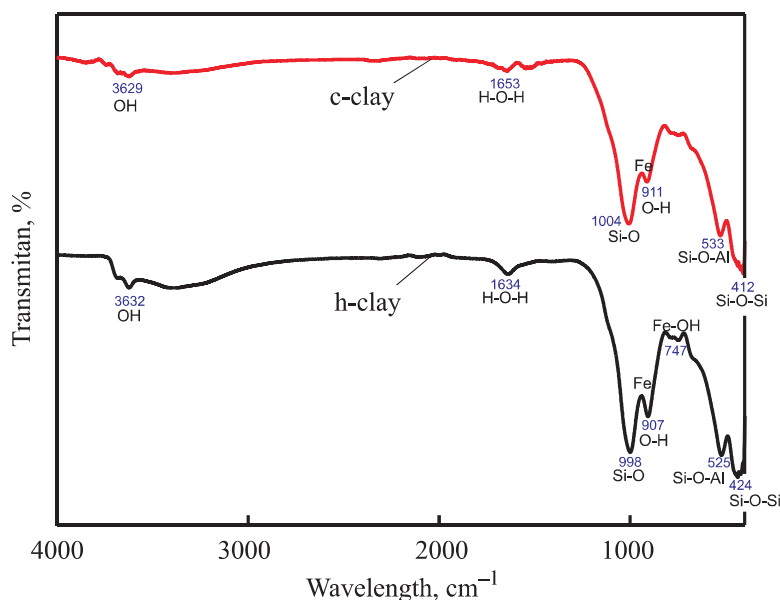

Fig. 2. Comparison of IR absorption patterns of h-clay and c-clay as measured by FTIR

molecules chemically bonded to the clay due to calcination [15]. The presence of metal in the clay was detected by the absorption at 907 cm^{-1} which shifted to 911 cm^{-1} where at this wave number there was a bending vibration of OH with cations. It is estimated that the cation that has a flexible vibration on absorption is Fe. Absorption of 747 cm^{-1} is also a stretching vibration of Fe–OH which is lost during calcination, meaning that the bond between Fe–OH is broken due to the evaporation of water which is chemically bound to clay minerals. Then the fingerprint area has absorptions, namely Si–O stretching vibrations, Si–O–Al bending vibrations, and Si–O–Si bending vibrations [16].

Effect of chemical treatment with two nickel salts. The ability of the above clay samples to undergo Ni^{2+} cations exchange was studied with XRF measurements. The parameters tested were the effect of reaction temperature and the type of nickel salt anion. It can be seen in Fig. 3 that nickel has ability in replacing other metals in clay, especially iron, probably because the ionic radius of Ni^{2+} is relatively not much different from that of Fe^{3+}. Based on this XRF data, we can also see that the layer network of clay minerals does not change significantly with the entry of nickel ions.
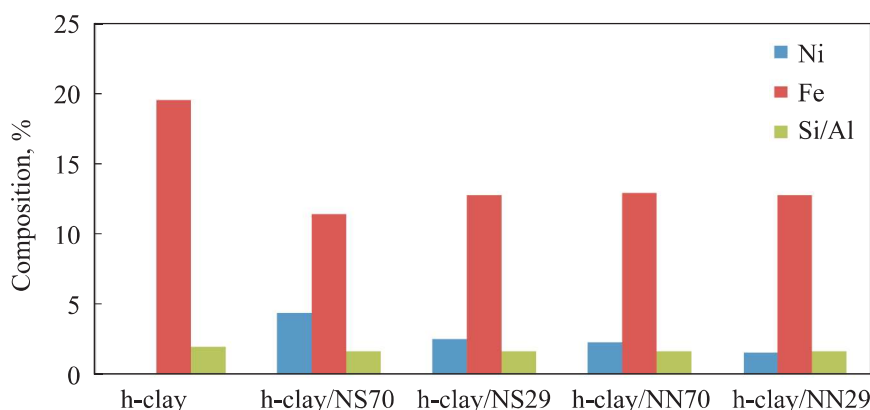
Fig. 3. Comparison of the performance of h-clay and c-clay in loading Ni^{2+} ions from their two salts at different temperatures

The effect of temperature is very significant where treatment at a higher temperature ignites the reaction rate faster because the increase in kinetic energy causes more opportunities for collisions and the movement of ions is also more rapidly. It is also shown in Fig. 3 that at 70 °C the loading capacity of the clay on nickel cations is about two times greater than that of the treatment the clay at room temperature. Both of these anions are classified as Weakly Coordinator Anions (WCA) which are very important in catalytic process to increase the reactivity of their metal cations [17]. We can also observe that sulfate ions

favor the ease of entry of nickel ions into the positive side of clay minerals due to the mole ratio between cations and anions in the two nickel salts. In nickel sulfate, the ratio of moles of cations and anions is 1 : 1 while in nickel nitrate it is 1 : 2, it is assumed that nickel ions from nitrate salt solution are more difficult to interact with the positive side of clay minerals because the higher number of nitrate anions also inhibits the nickel loading process.

Catalytic activity and selectivity. Studies of the catalytic activity of all clays prepared in this work including h-clay, c-clay, h-clay/NS70 and h-clay/NN70 were carried out in the transesterification reaction of palm oil with methanol to produce methyl esters which is also known as FAME. In comparison, nickel sulfate and nickel nitrate salts were also tested for their catalytic properties in the same reaction. The resulting methyl esters were measured qualitatively and quantitatively by GC-MS and all catalytic results are shown in Fig. 4.
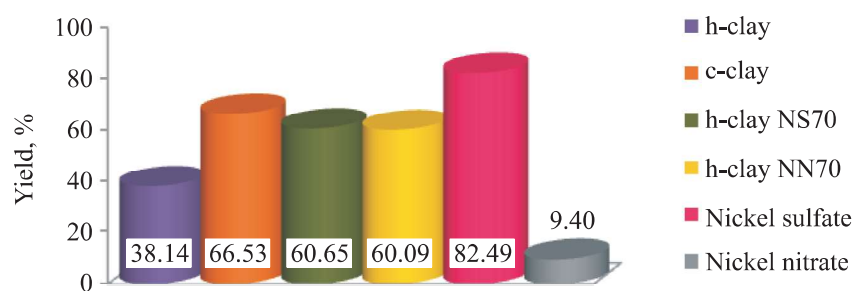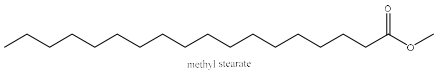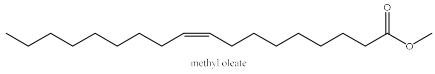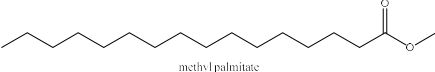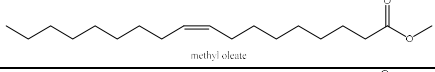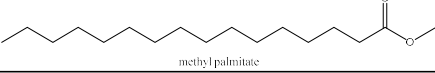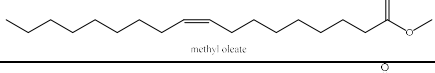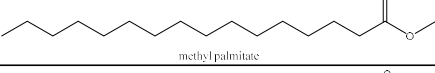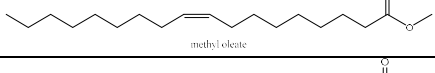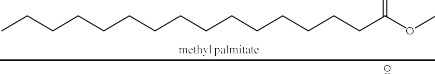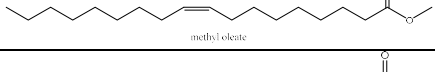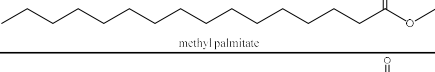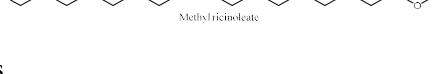

Fig. 4. Methyl ester yield of the tested catalyst

Using h-clay as a catalyst, it was produced 38 % methyl ester. The moderate catalytic ability of h-clay in the transesterification reaction is due to the presence of several cations naturally occurring in the clay such as calcium, potassium and sodium ions. After being treated thermally (c-clay) and chemically (h-clay/NS70 and h-clay/NN70) the performance of the clay increased significantly. C-clay also turned out to give more methyl ester products than h-clay/NS70 and h-clay/NN70. The calcination process which results in an increase in the kaolinite and illite phases seems to have a more positive effect on increasing the amount of methyl ester produced than the impregnation of nickel ions in the clay. As can be observed in almost all catalytic systems, in this study nickel sulfate as the homogeneous catalyst in the palm oil transesterification process also showed the highest yield of around 80 %. It is quite interesting to discuss especially nickel nitrate which only produces about 9 % of methyl ester. The effect of the presence of two parts of anions surrounding one part of cations on nickel nitrate is likely to narrow the opportunity for methanol to access nickel ions, which is known as space obstruction.

In terms of catalytic selectivity, as can be seen in Table 2, all clay-based catalysts tested in this work gave almost the same amount of saturated and unsaturated FAME. This is a challenge for the development of further research on how to produce more saturated FAME which is more suitable for biodiesel fueled engine [16].
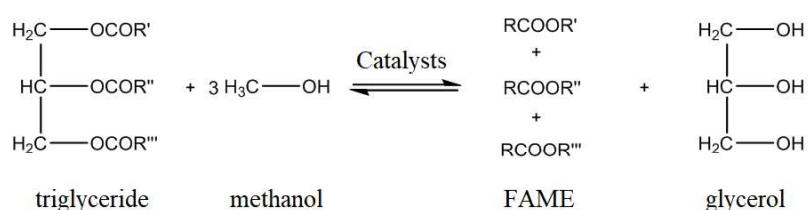
Table 2

Comparison of the catalytic selectivity of all clay-based catalysts tested in this study

Cata-lysts	Area, %*	FAME	Molecular structure	Saturated : unsatu-rated FAME*
h-clay	36.13	Methyl stearate	methyl stearate	54 : 46
	31.28	Methyl oleate	methyl oleate	
c-clay	40.88	Methyl palmitate	methyl palmitate	49 : 51
	59.12	Methyl oleate	methyl oleate	
h-clay/ NS70	38.01	Methyl palmitate	methyl palmitate	49 : 51
	39.03	Methyl oleate	methyl oleate	
h-clay/ NN70	37.03	Methyl palmitate	methyl palmitate	45 : 55
	46.05	Methyl oleate	methyl oleate	
Nickel sulfate	53.35	Methyl palmitate	methyl palmitate	53 : 47
	46.65	Methyl oleate	methyl oleate	
Nickel nitrate	1.54	Methyl palmitate	methyl palmitate	14 : 86
	1.11	Methyl oleate	methyl oleate	
	8.28	Methyl ricinoleate	Methyl ricinoleate	

* Data from GC-MS measurements.

The quality of the methyl ester produced in this study was only examined for density and found to be around 860 kg/L at 40 °C for all methyl ester yielded. The methyl esters obtained was in accordance with the Indonesian National Standard of 850–890 kg/L. Theoretically, a low density of such biodiesel will produce a high calorific value. When compared with the density of palm oil used as raw material, there is a very sharp decrease. Palm oil has a density of 890 kg/L (at 40 °C), after the transesterification reaction the density of the oil reduced significantly to 860 kg/L due to the breaking of the triglyceride chain to form FAME by the following reaction:

$$\underset{\text{triglyceride}}{\begin{array}{c} H_2C\text{——}OCOR' \\ | \\ HC\text{——}OCOR'' \\ | \\ H_2C\text{——}OCOR''' \end{array}} + \underset{\text{methanol}}{3\,H_3C\text{——}OH} \underset{\text{Catalysts}}{\rightleftharpoons} \underset{\text{FAME}}{\begin{array}{c} RCOOR' \\ + \\ RCOOR'' \\ + \\ RCOOR''' \end{array}} + \underset{\text{glycerol}}{\begin{array}{c} H_2C\text{——}OH \\ | \\ HC\text{——}OH \\ | \\ H_2C\text{——}OH \end{array}}$$

Conclusion. XRD measurements show that the main mineral composition of clay samples obtained from one location in Bukittinggi, West Sumatra, is illite and kaolinite. Analysis by XRD, XRF and FTIR of thermally treated clays showed a slight recomposition of clay minerals but no significant changes were observed in the Si/Al mole ratio after calcination. Thermal (calcination) and chemical (loading of nickel from two different salts) treatment to the clay seems to give a better yield of methyl esters than those non treated clay with an increase in methyl ester yield of between 20–30 %. Thermal treatment was also found to give slightly better catalytic effect than chemical treatment. When compared with their homogeneous counterparts, nickel sulfate and nickel nitrate, different results are seen where the sulfate salt gives the best catalytic yield of up to 80 % but the nitrate salt actually shows very low catalytic activity, only about 9 %.

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