



## A catalytic test of Mn(II) and Ni(II) grafted on modified mesoporous silica in transesterification of vegetable oil

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### ABSTRACT

The catalysts Mn(II) and Ni(II) which grafted on mesoporous silica has been tested in the transesterification of vegetable oil. Mesoporous silica was modified with bor trifluoride to obtain stronger electrostatic interaction between the metal and the support. As such, the amount of metal that can be loaded on the modified silica to metal Mn and Ni respectively 32 and 29%. Both types of catalysts tested in transesterification of vegetable oil with a mass ratio of catalyst : oil is 5 : 95. The total amount of the methyl ester product for both catalysts tested were ~13% for catalyst Mn (II) and ~5% for Ni (II) catalyst and still need to be examined at their optimum condition.

**Keywords:** Catalyst, mesoporous silica, metal loading and transesterification

### INTRODUCTION

Transition metals of manganese and nickel is commonly known to have catalytic properties. Manganese (II) acetonitrile for example, has been tested to increase the rate of polymerization of isobutene [1] while nickel is also famous as a catalyst in the hydrogenation [2]. The catalysts of transition metals in homogeneous phase are generally more active than the heterogeneous phase. However, the problem that arises is the difficulty of separating the catalyst with the product formed. The most frequent way that has been done to solve the problem is to combine the transition metal ions with material support in order to obtain a heterogeneous catalyst which is more easily separated from the reaction product. Silica has been the best choice in recent years for use as a support because it is relatively inert, thermally stable and economically cheap [3].

Silica has been the best choice in recent years for use as a support because it is relatively inert, thermally stable and large surface area. To improve the properties of the support, various approaches have been made to enlarge the surface area by multiplying the pores of silica, strengthen the bond between the metal with silica and others [4]. Catalytically, good support is able to load the metal in large quantities. Another requirement is not easily detached from the metal support. In the previous study we have prepared a porous support made of silica and chemically modified with BF<sub>3</sub>. In this report, the modified silica used as a support for manganese and nickel and its catalytic activity was tested in the reaction of transesterification of vegetable oils. Transesterification reaction becomes interesting lately because methyl ester product can be used as biodiesel. Typically, the reaction is catalyzed by acid (such as sulfuric acid) or base (such as metal alkoxides and hydroxides) [5]. On the other hand, Indonesia is known a country that is very rich in various plants as a source of vegetable oil to produce biodiesel reagents.

## EXPERIMENTAL SECTION

### Chemicals and reagents

The catalysts are manganese (II) and nickel (II) supported modified mesoporous silica obtained from previous research. For this report, we design each catalyst as Mn-SiO<sub>2</sub> and Ni-SiO<sub>2</sub>. Source of triglycerides is a commercial vegetable oil. Methanol is used without any previous purification process.

### Typical procedure for transesterification of vegetable oils


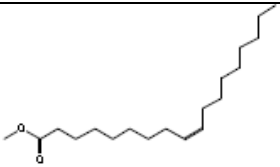
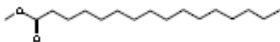
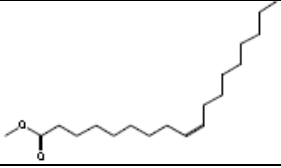
Reaction was prepared by setting the mass ratio between the Mn-SiO<sub>2</sub> catalyst with vegetable oil are 1:99; 2:98; 3:97; 4:96; 5:95 and 0:100. For a typical reaction, it was prepared by setting the mass ratio between the Mn-SiO<sub>2</sub> catalyst with vegetable oil is 1: 99. The first stage is the mixing of the catalyst with methanol by refluxing for 15 minutes at 60 °C. Then, the vegetable oil is added to the mixture and the reflux continued for the next 2 hours with stirring speed of 300 rpm. The reaction was stopped and the mixture is kept at room temperature for a while and transferred to a separating funnel and then left for another 24 hours. After that duration, the mixture which forms two boundaries separated and the upper layer is collected. The same procedures are also applied for another four ratio catalyst-vegetable oils. In the end, the mass ratio has the highest upper layer volume chosen to be investigated by GC-MS. In this research the mass ratio catalyst-vegetable oils with 5 : 95 is found to have the highest upper volume. The same procedure was also performed for the catalyst Ni-SiO<sub>2</sub> and it can be seen that the same ratio play significant role to yield the highest upper layer volume.

## RESULTS AND DISCUSSION

From the results we can observe that the Mn-SiO<sub>2</sub> and Ni-SiO<sub>2</sub> tested in the transesterification of vegetable oils are not very active to trigger more products methyl ester. This fact is due to the process being carried out not in their optimum condition because the aim of this work only to investigate whether the catalyst could catalyze the conversion of the oil to form biodiesel.

There are two types of methyl esters produced by both catalysts i.e. hexadecanoic methyl ester and 9-octadecanoic methyl ester (Table 1). In general, the manganese catalyst tends to have more total methyl ester (~13 %) than the nickel one which has only ~5 %. We can also conclude that the manganese catalyst is more likely to produce methyl ester containing double bonds that are familiar as oleic acid methyl ester. To control the reaction both catalysts are also compared with the reaction without the addition of such accelerators and it has been seen that the upper volume collected is much smaller than the one with catalysts.

**Table 1. Two products methyl ester of the catalysts Mn-SiO<sub>2</sub> and Ni-SiO<sub>2</sub> observed by GC-MS**

No.	Catalyst	Methyl Ester	Chem. Structure	Area (%)*
1	Mn-SiO <sub>2</sub>	Hexadecanoate		2.82
		9-octadecanoate		10.35
2	Ni-SiO <sub>2</sub>	Hexadecanoate		2.04
		9-octadecanoate		3.21

In the discussion of the catalytic activity of transition metals, properties such as the state of d orbitals, levels of oxidation, the maximum coordination number that can be achieved and the three dimensional structure of the complex plays an important role in the catalytic activity [6]. Another thing that can affect the reactivity of the catalyst in the form of complex compounds is ligands strength and ion pairs [7]. The basic properties of d orbitals of manganese (II) which has more unpaired electrons seem to play more role than the nickel (II) which only has two unpaired electrons thus affecting its ability to increase the amount of methyl ester which has a double bond in a long chain. It is also can be explained based on the concepts of catalytic above why in the case of Mn-SiO<sub>2</sub> the number of methyl ester products that contain double bonds are more favorable than the one with saturated chain.

### CONCLUSION

A manganese and nickel metals with oxidation state 2 supported by BF<sub>3</sub> modified mesoporous silica has been tested for transesterification of vegetable oils. The obtained products were measured with GC-MS. It can be concluded that both catalyst have low catalytic activity in such esterification process. The manganese catalyst has proven to be more active yielding 13 % of total methyl ester products than the nickel with only 5 %. It is also found that the manganese catalyst more favorable to produce unsaturated methyl ester compared to the nickel one.

### REFERENCES

- [1] Ayyamperumal Sakthivel, Ahmed K. Hijazi, Hui Yee Yeong, Klaus Köhler, Oskar Nuyken and Fritz E. Kühn, *J. Mater. Chem.*, **2005**, 15, 4441-4445
- [2] Homer Adkins, and Howard I. Cramer, *J. Am. Chem. Soc.*, **1930**, 52 (11), 4349–4358
- [3] Ayyamperumal Sakthivel, S. Syukri, Ahmed K. Hijazi, and Fritz E. Kuehn, *Catalysis Letters*, **2006**, 111(1–2), 43-47.
- [4] Syukri Syukri, Christian E. Fischer, Akef Al Hmaideen, Yang Li, Ying Zheng, and Fritz E. Kuehn, *Microporous and Mesoporous Materials*, **2008**, 113, 171–177.
- [5] Ricardo Serchelia, and Rogério Matheus Vargas, *J. of Braz. Chem. Soc, a Review Ulf Schuchardta*, **1998**, 9 (1), 199-210
- [6] Chaterine E. Hosecroft and Alan G. Sharpe, *Inorganic Chemistry*, second edition, *Pearson Ed. Lim*, England, **2005**, 786-808
- [7] Syukri Syukri, Ahmed K. Hijazi, Ayyamperumal Sakthivel, Akef I. Al-Hmaideen, Fritz E. Kuehn, *Inorganica Chimica Acta*, **2007**, 360, 197–202.