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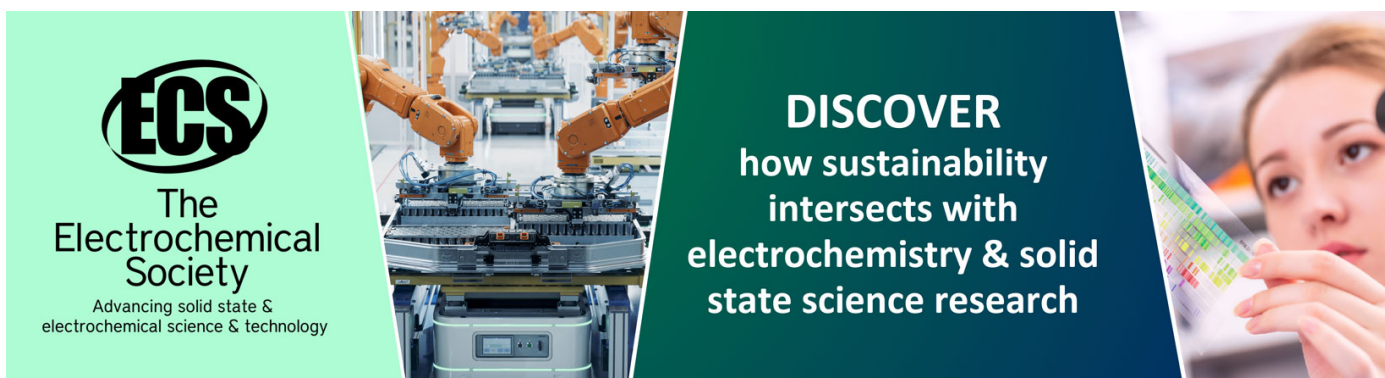
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Methoxylation of α -pinene using NiO/Y-Zeolite catalysts

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Abstract. α -Pinene in turpentine oil can be processed further to produce high value derivative compounds. One of the chemical process that can be used to increase of the value of α -pinene is by methoxylation by using certain catalysts. This study aims to determine the effects of time, temperature, and type of catalyst in the methoxylation of α -pinene. Characterization of the catalyst include: crystallinity by XRD (X-Ray diffractometer), the functional groups analysis by FT-IR (Fourier-Transform Infrared Spectroscopy), surface area of catalyst with SAA (Surface Area Analyzer), and the acidity test by gravimetric method. Modification of the catalyst with NiO does not change the crystal structure of Y-zeolite significantly. Methoxylation was carried out in a modified batch reactor with mixer at various temperatures 40, 50, 60°C and time variations for 1, 2, 3, 4 hours. Reaction products were identified by GC (Gas Chromatography) and GC-MS (Gas Chromatography Mass Spectrometry). The product of α -pinene methoxylation was found to be patchouli alcohol. The highest selectivity (67.06 %) and conversion (75.41%) were obtained at the temperature of 60°C and at reaction time of 4 hours with NiO/ZY catalyst. NiO/ZY catalysts is more selective to be used in the α -pinene methoxylation compared with H-ZY.

1. Introduction

Turpentine oil was known as paint solvents and it has low price. But α -pinene that contained in turpentine oil if processed further could produce other compounds of high value. Compounds derived from α -pinene can be used as raw material for the perfume industry, cosmetics, pharmaceuticals, and disinfectants [1,2]. α -pinene can be synthesized into a variety of other derivative compounds through chemical reactions with catalytic processes [3,4].

One of the chemical process that can be used to increase the value of α -pinene is methoxylation, which is the reaction of synthesizing ether using methoxy ion. The reaction will result α -terpinyl methyl ether, a compound that can be used as flavors and aromas for perfumes and cosmetic products, as an additive for pharmaceuticals and agricultural purpose, and is also used in the food industry [3,5]. However, until now, the research of α -pinene methoxylation is still rare.

Some of the catalysts have been used to process chemical reactions in the form of homogeneous catalysts and heterogeneous catalysts. The advantages of heterogeneous catalysts are easily separated from the liquid phase, not harmful to the environment, and reusable [6]. The use of solid acid catalysts in the hydration/isomerization α -pinene has been studied recently. But high selectivity with the possibility of a good activity difficult to be reached because α -pinene can be easily isomerized into many products [4].

Catalysts widely used in the chemical industry is transition metal such as Pt, Pd, Ni, Zn, Cd and etc [7]. Disadvantages of a metal catalyst is the active component clotting can occur when metal catalytic process takes place, resulting in shorter catalyst life. The problem addressed by elicits a metal catalyst on a support



material such as silica-alumina, alumina, activated carbon, or zeolite thus increased catalyst life. Y-zeolite functions as a bearer of the transition metals, one of them is Ni metal.

This study aimed to study the methoxylation of α -pinene into α -terpinyl methyl ether using Y-zeolite catalysts and Y-zeolite modified with NiO. Such modifications of Y-zeolite are expected to increase the activity of the Y-zeolite catalyst in the methoxylation α -pinene.

2. Research Methods

2.1. Materials and Instruments

The tools used in this study was an oven, a set of fractional distillation under reduced pressure, furnace, XRD (Shimadzu XRD-6000), GC (Agilent 6820), FT-IR (Perkin Elmer spectrum 100), GC-MS (Shimadzu QP- 5000), and SAA (Quantachrome NOVA 1200E). Turpentine oil, Y-zeolite (Sigma Aldrich), demineralized water, ammonia, Na_2SO_4 anhydrous, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, dried methanol (all pro analyst Merck).

2.2. Preparation of the Catalysts

Y-zeolite calcined at temperature of 550°C for 1 hour to prepare NiO/ZY. 2 g of Y-zeolite was added with $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (10%) which was dissolved in 20 mL aqua, then stirred at 80°C to form a slurry mixture, and dried in an oven at 110°C overnight. The $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ /Y-zeolite mixture calcined again at 550°C for 5 hours, thus formed NiO/ZY as described previously by Widiarti [8]. Next, several assessment was conducted such as crystallinity by using XRD, surface area by SAA, and functional groups analysis by FT-IR. As for the H-ZY catalysts, Y-zeolite was calcined for 5 hours at 550°C .

2.3. Methoxylations of α -pinene

The reaction took place in a modified batch reactor with a mixer at various temperatures, are 40, 50, 60°C . The reactor was filled with 10 mL of methanol (dried) and 0.5 mL α -pinene (99%), added with 0.5 g of the catalyst, and stirred with a mixer. The samples were taken at regular intervals on reaction time of 1, 2, 3 and 4 hours. The reaction product was assessed by using GC, GC-MS and FT-IR [3].

3. Results and Discussions

Catalysts H-ZY or NiO/ZY was characterized by XRD to determine the crystal structure of H-ZY and NiO/ZY. The results of diffractogram H-ZY and NiO/ZY is shown in Figure 1.

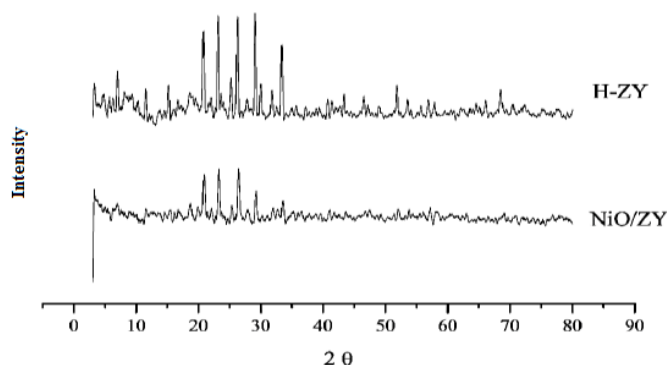


Figure 1. Diffractogram of H-ZY and NiO/ZY catalysts

Figure 1 indicated that the diffraction pattern between the H-ZY and NiO/ZY showed no shifting, but the intensity has decreased. The decrease was due to the intensity of falling metal would experience more thermal processes that can affect metal dispersion and distribution in the catalyst [9]. Despite the decrease in intensity, the crystal structure did not alter significantly.

Figure 1 also shows some typical peak at $2\Theta = 20,7^\circ$, $23,1^\circ$, $26,2^\circ$, $29,1^\circ$, and $33,3^\circ$. Suci (2016) have performed the synthesis of Y-zeolite and acquired distinctive peaks at $2\Theta = 6,2^\circ$, $10,1^\circ$, $11,8^\circ$, $20,2^\circ$, $23,5^\circ$, $26,9^\circ$, $30,5^\circ$, $31,2^\circ$, and $32,2^\circ$ [10]. Characterization of H-ZY and NiO/ZY catalysts were performed by using FT-IR analysis (Figure 2).

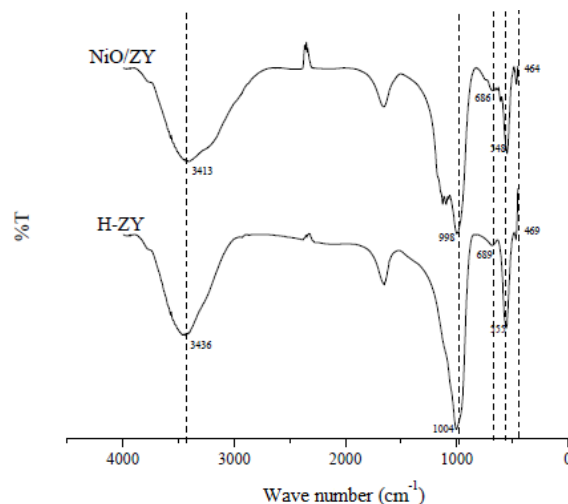


Figure 2. IR spectrum of H-ZY and NiO/ZY catalysts

Figure 2 shows absorption of functional groups on the H-ZY, including O-H stretching absorption at wave number 3436 cm^{-1} , the asymmetric stretching vibration of O-Si-O / O-Al-O at 1004 cm^{-1} , stretching vibration symmetry O-Si-O / O-Al-O at 689 cm^{-1} , double ring at 555 cm^{-1} , and the Si-O bending vibration / Al-O at wave number 469 cm^{-1} . While on NiO/ZY also appeared some functional groups that are not much different from the absorption of H-ZY. At the NiO/ZY catalyst, appeared OH stretching absorption at wave number 3434 cm^{-1} , stretching vibration asymmetry O-Si-O/O-Al-O at 998 cm^{-1} , stretching vibration symmetry O-Si-O / O -al-O at 686 cm^{-1} , double ring at 548 cm^{-1} , and the Si-O bending vibration / Al-O at wave number 464 cm^{-1} [11].

The surface area of the catalyst is determined by using the SAA (Surface Area Analyzer) by BET (Brunauer, Emmett and Teller) method. This analysis aims to determine the active surface area of the Y-zeolite catalyst impregnated with NiO. BET characterization results are shown in Table 1.

Table 1. Results of the characterization of surface area catalyst

Catalyst	Specific Surface Area (m^2/g)
H-ZY	20,78
NiO/ZY 10%	17,23

The more metal that falls to the solid catalyst will affect the specific surface area of the catalyst. The more amount of metal (NiO) used, there will be competition of diffusion into the pore mouth [12,13]. The decrease in the surface area above may also occur due to the uneven process of dispersing the metal NiO into the pore Y-zeolite and the accumulation of metal resulting in the closing of the pore Y-zeolite channel.

Temperature and reaction time exhibit effects on the rate of reaction. In kinetics, reaction rate increases with increasing temperature and reaction time. The results of GC-MS analysis showed are some compounds formed 3-cyclohexene 1-carboxaldehyde 1,3,4-trimethyl, patchouli alcohol and hexadecanoic acid. The highest compound represented by patchouli alcohol, so it is possible that most of the product formed from the reaction of methoxylation α -pinene is patchouli alcohol. This is also supported by the results of FT-IR analysis, which can be observed in Figure 3.

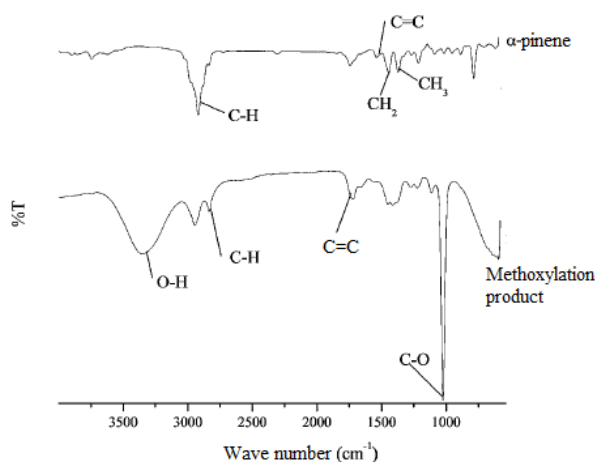


Figure 3. The infrared spectrum of the results of α -pinene methoxylation

Figure 3 provided some typical functional groups of the compounds resulted from α -pinene methoxylation. The O-H and C-O absorption appeared at wave number 3351 cm^{-1} , and 1024 cm^{-1} , respectively. Furthermore, alkenes aliphatic C-H appeared at wave number 2835 cm^{-1} and C = C functional group at wave number 1720 cm^{-1} . For O-H and C-O is the absorption of the alcohol compounds, while the functional groups of C-H and C = C is the absorption of alkenes [14]. It can be concluded that the substance produced from methoxylation of α -pinene is a type of alcohol and alkene compounds. Results of α -pinene methoxylation using H-ZY and NiO/ZY catalyst with variations in temperature and the reaction time was analyzed by GC and presented in Table 2.

Table 2. Results of methoxylation α -pinene using H-ZY and NiO/ZY catalyst

Catalyst	T (°C)	t (hour)	Conversion (%)	Selectivity (%)	Product		
					α -pinene (%)	Patchouli alcohol (%)	Other compounds (%)
H-ZY	40	1	58,53	63,04	41,09	36,90	22,01
	40	2	60,43	62,98	39,21	38,06	22,73
	40	3	62,08	62,96	37,58	39,09	23,33
	40	4	62,35	62,97	37,31	39,27	23,42
	50	1	60,76	62,26	38,89	37,83	23,28
	50	2	69,35	62,13	30,38	43,08	26,54
	50	3	69,56	62,46	30,17	43,45	26,38
	50	4	69,22	62,96	30,50	43,58	25,92
	60	1	66,51	62,81	33,19	41,77	25,04
	60	2	69,12	62,75	30,60	43,37	26,03
	60	3	71,98	62,78	27,76	45,19	27,05
	60	4	75,41	63,96	24,37	48,23	27,40
NiO/ZY	60	1	57,78	62,90	41,84	36,35	21,81
	60	2	53,10	63,28	46,48	33,60	19,92
	60	3	62,05	62,95	37,61	39,06	23,33
	60	4	59,67	67,06	39,97	40,01	20,02

Table 2 shows that the greater the temperature and reaction time used in α -pinene methoxylation with H-ZY catalyst and NiO/ZY catalyst, the α -pinene levels decreased. As for the content of patchouli alcohol

has increased and decreased, it is possible because during the reaction, another unknown compound may have been developed. Decreased levels of α -pinene is highest at the temperature of 60°C, the reaction time of 4 hours with H-ZY catalyst is equal to 24.37%. Patchouli alcohol concentration at 60°C and 4 hours of reaction time with the NiO/ZY catalyst is equal to 40.01%.

Temperature and reaction time used to carry out the α -pinene methoxylation with H-ZY catalyst overall influence on the desired result, the conversion, and selectivity. Optimal conversion of the reaction time at each temperature are presented in Figure 4a. The optimal temperature and reaction time on the product selectivity can be seen in Figure 4b and Figure 4c.

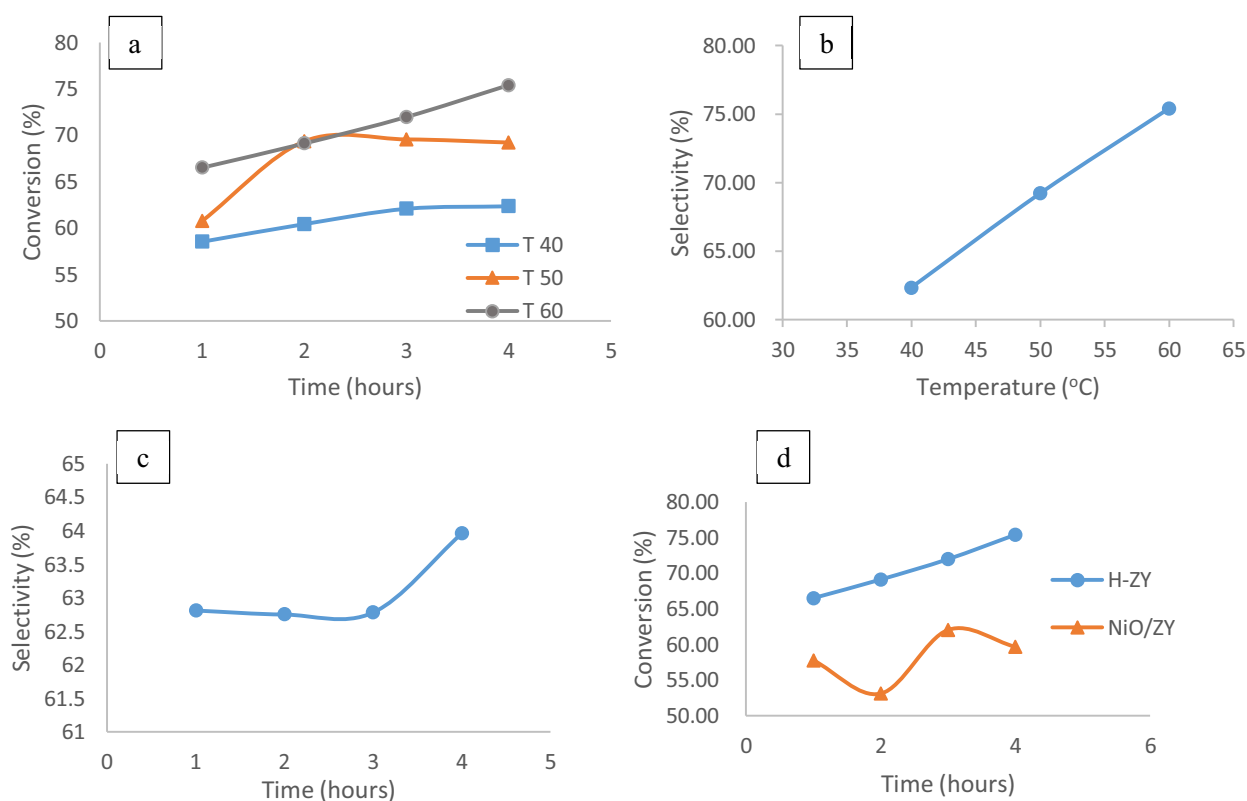


Figure 4. (a) Effect of reaction time on the conversion of α -pinene at a temperature of 40, 50 and 60 °C; (b) Effect of temperature on product selectivity in the reaction time of 4 hours; (c) Effect of reaction time on product selectivity at temperature of 50 °C; (d) Effect of reaction time on the conversion of α -pinene decline at a temperature of 60°C with a catalyst NiO/ZY and H-ZY.

Figure 4a shows the higher the temperature and the longer reaction time, the conversion of α -pinene is decreased. Optimal conversion obtained at a temperature of 60 °C and a reaction time of 4 hours with H-ZY catalyst that is equal to 75.41%. From Figure 4b, it is known that at reaction time of 4 hours, the selectivity of the product has increased from a temperature of 40°C to 60°C. Actually, research has also been carried out at a temperature of 70°C, but before reaching 70°C, reactants have reached the boiling point so the product was not produced at that temperature. Optimal temperature obtained on reaction time 4 hours, with H-ZY catalyst at a temperature of 60°C, and with a product selectivity of 63.96%.

Figure 4c shows the effect of reaction time on product selectivity with H-ZY catalyst. The reaction runs at a temperature of 60 °C for 1 hour, 2 hours, 3 hours and 4 hours. The selectivity decreased slightly from 1h to 2h, then increased at 3h to 4h. In this study, the optimal reaction time is obtained when the temperature is 60°C for 4 hours with a selectivity of 63.96%. While the comparison of the results of α -pinene conversion

with H-ZY and NiO / ZY catalysts presented in Figure 4d. Figure 4d shows increased conversion of α -pinene with H-ZY catalyst at a temperature of 60°C, while the catalyst NiO / ZY at 60°C was fluctuative. The decrease is due to the conversion of methoxylation is a reversible reaction. This is in line with previously conducted research by Salamah (2014) regarding transesterification, that the transesterification is a reversible reaction so when the reaction has reached the optimum conditions, then the reaction will shift to the left (reactants) and would minimize products obtained [15]. Methoxylation with H-ZY produce higher conversion than the catalyst NiO/ZY. Comparison of selectivity with H-ZY and NiO/ZY catalyst presented in Figure 5.

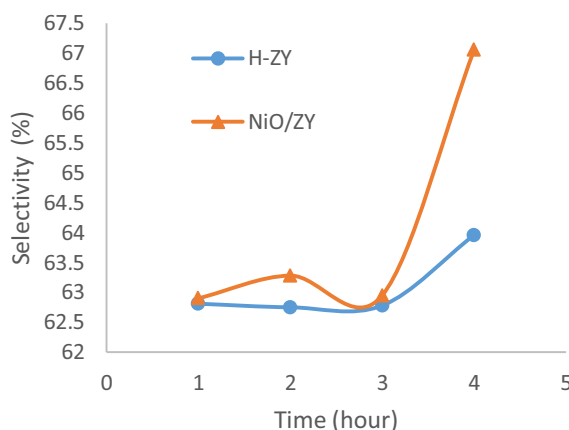


Figure 5. Effect of reaction time on product selectivity at temperature of 60 °C with NiO / ZY and H-ZY catalyst. Reaction conditions: α -pinene 0.5 mL, 10 mL of methanol and 0.5 g of catalyst H-ZY.

The selectivity of the H-ZY catalyst decreased at the reaction time 1 hour to 2 hours, then at reaction time 2 hours to 4 hours. While the selectivity with catalyst NiO/ZY is fluctuated. This decrease is caused because in this condition other compounds have formed. At the same conditions (temperature 60 °C and reaction time of 4 hours) selectivity with catalyst NiO/ZY (67.06%) was higher than the H-ZY catalyst (63.96%). This means the use of a catalyst which is carried by the metal (NiO/ZY) are more selective to produce a product.

According Catrinescu (2015), most compounds produced in the methoxylation are terpinyl methyl ether [3]. This is in contrast to the results of this study. Based on the data that has been obtained, it is known that most of the methoxylation product resulted in patchouli alcohol. Non-compliance results may be caused by ether compounds that should be a major product had undergo auto-oxidation without oxidized by reagents [14]. Another reason is that the methods of mixing reactants and catalysts are not precised, but it is also due to a less selective catalyst used to produce the desired product.

4. Conclusion

Temperature, reaction time and the type of catalyst affects the reaction yield methoxylation of α -pinene. Conversion α -pinene levels decrease exponentially over time, the highest conversion (75.41%) obtained at temperature 60 °C and at reaction time of 4 hours. As for the highest product selectivity (67.06%) obtained at temperature is 60 °C and at reaction time of 4 hours with the catalyst NiO/ZY. NiO/ZY catalyst is more selective for use in reaction α -pinene methoxylation, when compared with the H-ZY catalyst.

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