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Catalytic transformation of 1,8-cineole from Cajeput oil to *p*-cymene with modified zeolite beta catalyst

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Abstract. Catalytic transformation of 1,8-cineole from Cajeput oil was studied with Fe^{3+}-Zeolite beta and Ni^{3+}-Zeolite beta catalysts. 1,8-Cineole was obtained by fractional distillation under reducing pressure of Cajeput oil from Gundih Purwodadi. Preparation of Fe^{3+}-Zeolite beta and Ni^{2+}-Zeolite beta catalysts was conducted by ion exchange and calcination, followed by catalytic activity test on aromatization of 1,8-cineole reaction in acetic anhydride. Optimization of reaction condition was studied with variation of temperature, reaction time and reactant mole ratio. The purity of 1,8-cineole isolated from Cajeput oil was 84.81%. The best total activity and selectivity of Fe^{3+}-zeolite beta catalysts were obtained by molar ratio [SIN]/[AA] 1:4 at reaction times of 720 minutes of 69.66% and 20.47% respectively.

1. Introduction

Cajeput oil is one of the essential oils that obtained from the distillation of *Melaleuca spp*. leaves. Based on data from the Indonesian National Standard [1], it was shown that 1,8-cineole is the largest component of Cajeput oil which reaches 60%. 1,8-Cineole compounds or often called "cineole" are active pharmaceutical components of eucalyptus oil, referred to as "eucalyptol" in commercial trade [2]. Conversion of 1,8-cineole raw material using $Pd-2.Al_2O_3$ catalyst produced *p*-cymene as the main product of hydrophilic liquid and hydrogen as the main product of gas [3, 4]. 1,8-Cineole compound is the main chemical component of Cajeput oil. The cheaper of production cost makes cineole a very attractive raw material for industrial chemical production. Thus, it is not surprising that cineole is a potential renewable raw material for C_{10} industrial chemical production and chemical precursors such as *p*-cymene [5].

p-Cymene can be used as in the production of cresol, perfume, drugs, and herbicides [4]. In addition, *p*-cymene is an important chemical compound that is widely used for the synthesis of *p*-cresol, pharmaceutical industry and for the production of fungicides, pesticides, and flavouring agents [6]. Santana *et al.* [7] reported that *p-cymene* has high orofacial antinociceptive activity in rats.

Lewis acid catalysts have an oxidation role in the acetylative aromatization reaction of 1,8-cineole to *p*-cymene [8]. The use of heterogeneous catalysts can be an alternative in the chemical industry because it is easy to separate and the catalyst can be reused. The cost process of heterogeneous catalysts is generally lower than homogeneous catalysts, and is more environmentally friendly than homogeneous catalysts. According to Mäki-Arvela *et al.* [9] the synthesis of isopulegol compounds from citronellal using zeolite beta is more selective than other zeolites. The conversion after 3 h reaction time in the cyclization of (+)-citronellal is in the following order: H-Beta-11>H-MCM-41>H-ZSM-5>SiO_2. Activity of modified zeolite beta catalysts also studied in previous research [10, 11]. The zeolite beta is expected to be used as a carrier because it is stable in high heating, good porosity and a large surface

area. Fe^{3+} ion was chosen as the active precursor of the catalyst because the d orbitals are not fully filled so they can promote catalysis reactions [12]. The oxidation property was thought to play a role in the reaction of 1,8-cineole acetylative aromatization to *p*-cymene, therefore this study compared Fe^{3+}-Zeolite beta catalytic activity with Ni^{2+}-Zeolite beta. Kinetic studies were carried out to study the catalytic mechanism of the 1,8-cineole transformation reaction to p-cymene. According to Derouane *et al.* [13] the Langmuir-Hinshelwood mechanism model can be used to explain reaction kinetics and the mechanism of reactants and products for active sites on the catalyst surface.

2. Methods

2.1. Instruments and Materials
Isolation of 1,8-cineole using a set of fractional distillation under reducing pressure. Analysis of catalyst was conducted using X-Ray Diffraction (XRD) Rigaku miniflex 600, X-Ray Fluorescence (XRF) Bruker, Fourier Transform Infra-Red (FT-IR) 100 Perkin Spectrum Elmer, Agilent 6890 Gas Chromatography (GC) and Shimadzu QP2010S Gas Chromatography-Mass Spectrophotometer (GC-MS).

The materials used in this study were Cajeput oil from Perhutani Gundih, Central Java, Indonesia, zeolite beta (Tosoh Takasago), distilled water, $FeCl_3$, acetic, n-hexane, $AgNO_3$, $Ni(NO_3)_2.6H_2O$ grade pro analyst provided by Merck.

2.2. Experiment
The initial treatment of samples was analysing the eucalyptus oil using GC. Cajeput oil 250 mL was put into a distillation flask that containing boiling stones in the set of fractional distillation under reducing pressure. Distillate was collected into fraction 1 and fraction 2 at temperature 56-90°C and 90-156°C, respectively. Each fraction was analysed using GC. The most 1,8-cineole content fraction based on the results of GC analysis was redistilled and analysed using GC.

Catalyst preparation was carried out by means of NH_4^+-zeolite beta calcined at a temperature of 600°C for 5 hours to form active H-zeolite beta. Then 20 g of active H-zeolite beta were immersed in 100 mL 0.1 M $FeCl_3$ for 24 hours and stirred using a magnetic stirrer. The mixture was filtered using a Buchner filter and washed with distilled water to free Cl^- ions which were detected with $AgNO_3$ solution. Then the resulting Fe^{3+}-zeolite was dried at a temperature of 120°C for 3 hours and calcined at a temperature of 600°C for 5 hours. Fe^{3+}-zeolite beta catalyst was characterized its acidity parameters using the gravimetric method, its crystallinity using XRD, and its metal content using XRF. The same treatment was carried out to make the Ni^{2+}-zeolite beta catalyst with 0.1 M $NiNO_3$ solution.

The acetylative aromatization reaction was carried out by adding 1,8-cineole, acetic anhydride and Fe^{3+}-zeolite beta into a three-neck flask according to the parameters in table 1. The mixture was then refluxed at a temperature of 80°C. During the reaction, 1 mL of each sample was taken at the minute of 180; 360; 540; and 720 into a tube and then added 9 mL of n-hexane-water mixture (1:2) and separated using a centrifuge for 5 minutes at a speed of 270 rpm. The organic fraction was sampled and the solvent was evaporated by nitrogen gas. The results obtained were tested with GC and GC-MS.

The activity test of the Ni^{2+}-Zeolite beta catalyst was carried out by add 7.5 g (44.3 mmol) 1,8-cineole, 14 mL (148.2 mmol) acetic anhydride and (1) 1 g beta H-zeolite, (2) 1 g of Ni^{2+}-zeolite beta in a three-neck flask which was equipped with a cooling back, thermometer, magnetic stirrer, and nitrogen gas as atmosphere reaction. The mixture was then stirred and heated at a temperature of 80°C. 1 mL of samples were taken at the 4th, 8th, and 12th hour. Mixture of reaction product was put into the centrifuge test tube, adding by distillated water and n-hexane with a ratio of 2:1. Then the separation was conducted by centrifuge for 5 minutes at a speed of 270 rpm. The organic fraction was taken with a drop pipette, then put into a bottle.

Table 1. Experimental parameters of acetylative aromatization reaction of 1,8-cineole with Fe^{3+}-zeolite beta.

experimental parameters	A1	A2	A3	A4	A5
[SIN]/[AA]	1:4	1:2	1:1	5:4	3:2
1,8-cineole (mmol)	19.20	38.40	38.40	47.52	57.12
1,8-cineole (g)	2.96	5.81	5.81	7.33	8.81
Acetic andhydride (mmol)	76.17	76.17	38.08	38.08	38.08
Acetic anhydride (gtabel)	7.78	7.78	3.89	3.89	3.89
Catalyst Fe^{3+}-zeolite beta (g)	1	1	1	1	1

The reaction rate *(R)* is defined as the number of products (mmol) *p*-cymene produced per minute and per gram of catalyst. Then the graphs are created:

$$[1/R \; x \; [SIN]/[AA]] \; vs. \; [SIN] \; /[AA]$$

at the same reaction time t. The quadratic equation produced and must satisfy equation:

$$2 \; (ac) \; 1/2/b \; = 1 \tag{1}$$

Reaction rate constant was determined with equation the equation (2) was used.

$$k \; = \; 2/b \; \text{or} \; k \; = \; (ac) - 1/2 \tag{2}$$

Whereas in determining the comparison value of the 1,8-cineole equilibrium adsorption constant with acetic anhydride, equation (3) was used.

$$KSIN/KAA \; = \; 2a/b \tag{3}$$

3. Results and Discussion

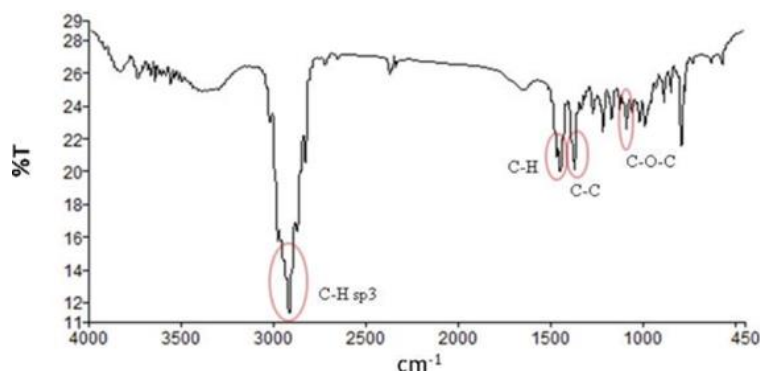### 3.1. Isolation of 1,8-cineole from Cajeput oil

Figure 1. IR Spectrum of 1,8-cineole which was isolated from Cajeput oil.

Isolation of 1,8-cineole from Cajeput oil was carried out by fractional distillation under reduced pressure. This was done to avoid oxidative decomposition of oil components by high temperatures. 1,8-cineole compounds have a relatively high boiling point of 174-177°C. Distillation fractions of Cajeput oil were analysed by GC. Its levels in fraction 1 (56-90°C) and 2 (90-156°C) were 77.26% and 38.93%. Fraction 1 of 1,8-cineole compound increased to 84.81% after being redistributed. The result of redistillation of fraction 1 was analysed by FTIR cineole which presented in Fig. 1. The IR spectrum in

Fig. 1 shows the stretching vibration of the C-H sp^3 group in the wave number 2921.22 cm^{-1}, the stretching of the CH group in the wave number region 1446.96 cm^{-1}, and vibrations stretching the ether group in the wave number region 1054.12 cm^{-1}.

3.2. Catalysts Characterization

Characterization of catalyst using XRD aims to analyse the crystallinity of the catalyst. The catalyst diffraction pattern can be seen in Fig. 2 which shows the relationship between intensity and 2θ.
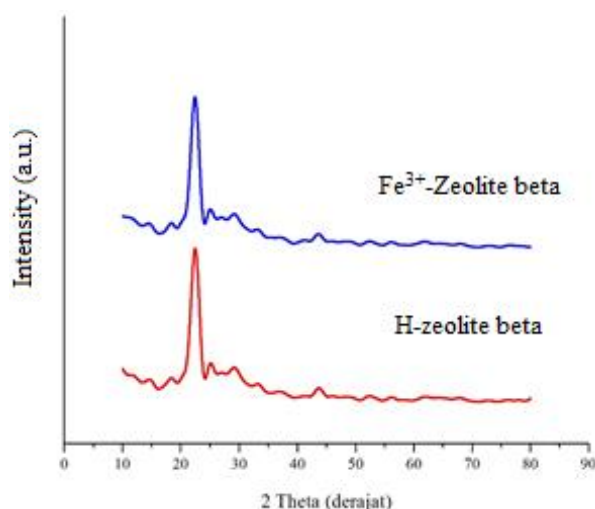

Figure 2. XRD diffractogram of H-zeolite beta and Fe^{3+}-zeolite beta.

The diffraction pattern of the two catalysts is almost the same, this means that structure of zeolite beta did not change by ion exchange process. Based on XRF data, it is also known that % Fe as Fe_2O_3 is 2.82%, Si/Al ratio at H-zeolite beta was 23.92 while in Fe^{3+}-zeolite beta is 41.18. The size of the Si/Al ratio was proportional to the acidity of the catalyst. The greater the Si/Al ratio, the more acidic. The data also shows that the Si ratio was greater so that it was Bronsted acid. This shows that Fe^{3+}-zeolite beta is more acidic than H-zeolite beta according to the results of the acidity test analysis using the gravimetric method. The acidity of the catalyst was determined using the gravimetric method, which was a measurement based on the difference in mass of the catalyst before and after absorbing the base. Catalyst acidity is related to the number of active sites in the catalyst. Modification with Fe^{3+} ion exchange increases acidity from 3.19 mmol/g to 3.40 mmol/g.

The diffraction pattern of NH$_4^+$-zeolite beta, H-zeolite beta, and Ni^{2+}-zeolite beta, can be seen in Fig. 3 which shows the relationship between intensity and 2θ. The diffraction pattern of the three catalysts is almost the same, but there is a shift in the value of 2θ from the resulting diffraction peak. This means that there has been a change in the catalyst due to catalyst activation and ion exchange and impregnation processes.
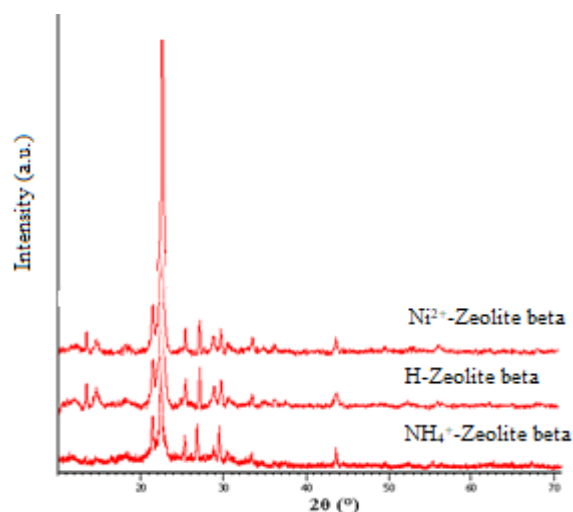
Figure 3. XRD diffractogram of NH^{4+}-zeolite beta, H-zeolite beta, and Ni^{2+}-zeolite beta.

Activation of NH_4^+ -zeolite beta into active H-zeolite beta by calcination at a temperature of 600°C causes an insignificant peak shift. This indicates that the calcination treatment at a temperature of 600°C did not change the solid structure as a whole. The change in intensity in some of the strongest peaks results in a change in the crystallinity of the catalyst after calcination at high temperatures. This result also indicates that the H-zeolite beta has a fairly high stability of the structure. The results of the analysis with XRF showed that Ni content as NiO in Ni^{2+}-Zeolite beta was 3.07% and an increase in Si/Al ratio from 23.92% to 27.00%. Total acidities measured by gravimetric method with NH_3 adsorption of beta H-zeolite and Ni^{2+}- zeolite beta were 3.1832 and 3.4748 mmol/g respectively. Based on the comparison of Si/Al ratio in catalyst analysis with XRF, it is known that there is a relationship between the increase in Si/Al value and the total acidity value of the catalyst. The higher the Si/Al value, the higher the total acidity value of the catalyst or the more acidic sites on the catalyst. With the increase in the acidic site, the activeness of the catalyst also increased.

3.3. Catalyst Activity Test

The acetylative aromatization reaction of 1,8-cineole produced with acetic anhydride to *p*-cymene using Fe^{3+}-zeolite beta catalyst was carried out at a temperature of 80°C. The reaction variation conditions include the mole ratio of reagents (1,8-cineole: acetic anhydride i.e. 1:4 (A1), 1:2 (A2), 1:1 (A3), 5:4 (A4), and 3:2 (A5)) and the reaction duration of 180, 360, 540, and 720 minutes. Each reaction result was analysed using GC. The yield of the reaction product is presented in Fig. 4.

Based on the data in Fig. 4 it is known that increase in the molar ratio [SIN]/[AA] decrease in the yield of *p*-cymene products. The decrease in the *p*-cymene yield along with the increase in the molar ratio [SIN]/[AA] was due to the less amount of acetic anhydride so that the acetylation agent in the reaction was less and the product produced was lower. The yield of the *p*-cymene product formed increases with the increase in the duration of the reaction. The reaction with the molar ratio [SIN]/[AA] 1:4 or A1 on the 720-minute reaction duration showed the best percentage of *p*-cymene yield which was 12.62%.

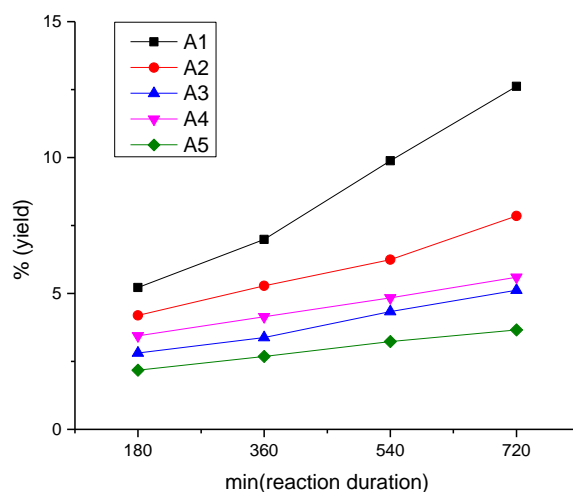**Figure 4.** Yield of *p*-cymene (%) on acetylative-aromatization reaction of 1,8-cineole with Fe^{3+}-zeolite beta in acetic anhydride.

Activity and selectivity of Fe^{3+}-zeolite beta on acetylative aromatization of 1,8-cineole could be find in table 2. Data on table 2 shows that activity of Fe^{3+}-zeolite beta catalyst on acetylative aromatization reaction of 1,8-cineole in acetic anhydride increases with increasing reaction duration in each molar ratio [SIN]/[AA]. The molar ratio of [SIN]/[AA] 1:4 or A1 on the reaction duration of 720 minutes gives the best total activity of 69.66%. The total product activity results obtained are relatively large. The best selectivity results for the formation of *p-cymene* products in the molar ratio of [SIN]/[AA] 1:4 or A1 with a reaction duration of 720 minutes at 20.47%. When compared with the best activity of 69.66% it can be seen that the Fe^{3+}-zeolite beta catalyst has good activity but poor selectivity to the aromatic acetylation-reaction of 1,8-cineole to *p*-cymene.

Table 2. Total activity (%) and *p*-cymene selectivity (%) in acetylative aromatization of 1,8-cineole with Fe^{3+}-zeolite beta in acetic anhydride at various molar ratios [SIN]/[AA].

[SIN]/[AA] Molar ratio	Activity (%)				Selectivity (%)			
	180 min	360 min	540 min	720 min	180 min	360 min	540 min	720 min
A1	49.43	62.05	67.99	69.66	10.06	11.49	15.69	20.47
A2	19.84	26.89	32.21	39.03	15.09	16.14	17.23	19.40
A3	20.97	27.71	34.34	40.63	9.29	9.56	10.82	11.51
A4f	15.06	18.39	24.85	30.39	14.05	15.55	15.40	15.84
A5	34.81	41.47	46.32	49.13	5.12	5.63	6.30	6.88

Analysis chromatogram GC of the products of acetylative aromatization reactions of 1,8-cineole with Ni^{2+}-zeolite beta is presented in table 3. These chromatograms were compared with its of pure *p*-cymene compounds.

Table 3. Yield of *p*-cymene (%) on acetylative aromatization reaction of 1,8-cineole with Ni^{2+}-zeolite beta in acetic anhydride.

Catalyst	Compound	% Yield at time of reaction		
		240 min	480 min	720 min
H-zeolite beta	1,8-cineole	64.42	56.31	52.10
	p-cymene	2.69	3.69	4.49
Ni^{2+}-zeolite beta	1,8-cineole	70.49	66.89	63.72
	p-cymene	3.10	3.89	4.56

Based on the reaction product it was known that modified of zeolite beta increased activity of catalyst but the catalyzed reaction of Ni^{2+}-zeolite beta showed lower activity than Fe^{3+}-zeolite beta. An extended reaction time of up to 24 hours for the catalyzed reaction of Ni^{2+}-zeolite beta showed an increase in the *p*-cymene product to 11.39%, identification components in the mixture of product reactions was carried out by GC-MS. Chromatogram analysis results with GC-MS QP2010S Shimadzu Rtxi 5MS non polar columns can be seen in Fig. 5.
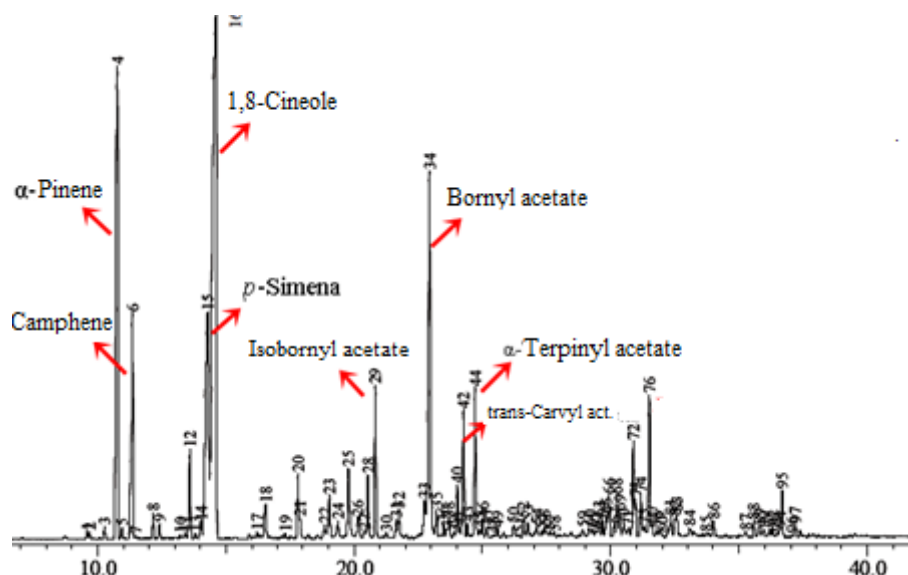
Figure 5. Chromatogram of acetylative aromatization reaction of 1,8-cineole with Ni^{2+}-zeolite beta in acetic anhydride at 24 h.

3.4. Kinetic study of acetylative aromatization of 1,8-cineole with Ni^{2+}-zeolite beta in acetic anhydride
Analogous to the reaction rate equation proposed by Derouane *et al.* [13], the acetylative aromatization-reaction rate of 1,8-cineole is defined as the number of products (mmol) of *p-cymene* produced per minute and per gram of catalyst. The reaction rates (R) and (1/R) ([SIN]/[AA]) at each reaction time duration are presented in table 4.

Table 4. Analysis of R vs [SIN]/[AA] and (1/R) ([SIN]/[AA]) vs. [SIN]/[AA] for each duration time of the 1,8-cineole acetylative aromatization with Fe^{3+}-zeolite beta in acetic anhydride.

[SIN]/[AA] Molar ratio	R (mmol/g.min)				(1/R)([SIN]/[AA])			
	180 min	360 min	540 min	720 min	180 min	360 min	540 min	720 min
A1	0.215	0.144	0.136	0.130	1.161	1.733	1.839	1.921
A2	0.173	0.109	0.086	0.081	2.894	4.599	5.833	6.190
A3	0.115	0.069	0.059	0.053	8.667	14.406	16.855	18.977
A4	0.142	0.086	0.067	0.058	8.783	14.605	18.755	21.603
A5	0.089	0.055	0.044	0.038	16.688	27.074	33.754	39.715

The reaction rate has decreased to increase the reaction duration to 720 minutes. The optimum conditions for the aromatization reaction of 1,8-cineole catalysed Fe^{3+} -zeolite beta occur in the molar ratio of [SIN]/[AA] 1:4 or A1 with a reaction duration of 180 minutes.

Graphs of quadratic equations from (1/R) ([SIN]/[AA]) to [SIN]/[AA] are used to formulate the comparison values of adsorption equilibrium constants and reaction rate constants. The quadratic equation obtained at each reaction time duration is presented in table 5.

Table 5. Analysis (1/R)([SIN]/[AA]) vs [SIN]/[AA] in acetylative aromatization of 1,8-cineole with the acetylative aromatization of 1,8-cineole Fe^{3+}-zeolite beta in acetic anhydride.

Reaction time (min)	Quadratic equation	$2(a.c)^{1/2}/b$
180	$y = 4.9711x^2 + 3.777x - 0.1438$	0.45
360	$y = 7.1954x^2 + 7.8513x - 0.8344$	0.63
540	$y = 10.703x^2 + 6.6801x - 0.39$	0.61
720	$y = 14.593x^2 + 4.5464x + 0.0099$	0.17

The quadratic equation in table 5 can be used in determining the reaction rate constant (kSIN/AA) and the ratio of the adsorption equilibrium constant (KSIN/KAA), if it meets the requirements of 2 (ac) 1/2b or equals 1. Based on these conditions, selected rate data with quadratic equations on reaction duration of 360 minutes with a value of 2 (ac) 1/2/b=0.63.

The rate constant is determined using the formula kSIN/AA=(2/b) or kSIN/AA=(a.c)-1/2. The value of kSIN/AA=(2/b) is 0.25 mmol/minute. Gram of catalyst, while the value of kSIN/AA=(a.c)-1/2 is 0.41 mmol/minute. The value of the comparison of the adsorption equilibrium constant of KSIN/KAA=(2a/b) is 1.83.

Based on the calculation, it is known that the aromatics-acetylative reaction rate constants of 1,8-cineole with acetic anhydride use Fe^{3+}-zeolite beta catalyst for a duration of 360 minutes of reaction time and a reaction temperature of 80°C is 0.25-0.41 mmol/min. catalyst. The value of KSIN/KAA is 1.83 indicating that 1,8-cineole adsorption on Fe^{3+}-zeolite beta catalyst is stronger than adsorption of acetic anhydride. This is presumably because the 1,8-cineole alkalinity level is greater than that of 1,8-cineole acetic anhydride is more strongly adsorbed on the acidic catalyst surface. The steric factor can also affect; 1,8-cineole has a larger molecular weight than acetic so that 1,8-cineole more covers the catalyst surface. The presence of free electron pairs on 1,8-cineole also causes 1,8-cineole to be more adsorbed on the catalyst surface, because the Fe^{3+}-zeolite beta catalyst is ionized to Fe^{3+} and H-zeolite beta. The presence of Fe metal which has unpaired electrons in the d orbitals becomes the free electron

pair acceptor on 1,8-cineole. The increase of the 1,8-cineole fraction on the catalyst surface prevents adsorption of acetic anhydride, at excessive amounts can even close the pores.

Based on kinetic data, the mechanism of the 1,8-cineole reaction with acetic anhydride uses the Fe^{3+}-zeolite beta catalyst according to the Langmuir-Hinshelwood approach. The reactants molecule, 1,8-cineole and acetic anhydride, is adsorbed on the catalyst surface active site. These two molecules of adsorbed reactant then react to form the product. The resulting product is then dissipated from the catalyst surface.

4. Conclusion

Modification of zeolite beta by ion exchange increases solid acidity but did not change the structure zeolite beta significantly. Ion exchange also showed increased activity of catalyst but the catalysed reaction of Ni^{2+}-zeolite beta showed lower activity than its of Fe^{3+}-zeolite beta. Based on kinetic study, the mechanism of the 1,8-cineole reaction with acetic anhydride uses the Fe^{3+}-zeolite beta catalyst according to the Langmuir-Hinshelwood approach. The reactant molecule, 1,8-cineole and acetic anhydride, were adsorbed on the catalyst surface active site. These two molecules of adsorbed reactant then react to form the product. 1,8-cineole also causes 1,8-Cineole more adsorbed on the catalyst surface than acetic anhydride.

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