A Kinetics study of 2-ethyl-2-hexenal hydrogenation to 2-ethyl-hexanol over Nickel based catalyst

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Abstract. The 2-ethyl-hexanol was much-needed in the plasticizer industry as a precursor for the synthesis of bis diesters (2-ethyl hexyl) phthalate (DEHP). This compound can be synthesized by oxo reaction, where one of the steps is a consecutive hydrogenation of the 2-ethyl-2-hexenal to 2-ethyl-hexanol. This reaction required metal-based catalyst. This research aimed to develop the formula and procedure of catalyst synthesized and get a kinetics of the reaction. The catalyst was synthesized with a nickel content of 50%-w. The support consists of γ-alumina and SiO2(cab-osil) in variations of 0%-w up to 100 %-w of cab-o-sil towards support. The activity of synthesized catalysts were tested at 120°C and 30 bars in the fixed bed reactor. The results showed that the best performing catalyst was NiO50-Cab50 with 98.29% 2-ethyl-2-hexenal conversion and selectivity to 2-ethyl-hexanol 87.41 %. By varying the reaction temperature of 100-120°C in the best catalyst, it is found that the consecutive reaction was the first order with the activation energy of 2-ethyl-2-hexenal hydrogenation to 2-ethyl-hexanol was 33.66 kJ/mol and hydrogenation 2-ethyl-hexenal to 2-ethyl-hexanol was 58.39 kJ/mol. This showed that the hydrogenation of C = C bonds was easier than the C = O bond.

1. Introduction
The 2-ethyl-hexanol compound was required in the plasticizer industry as a precursor for the synthesis of bisdiesters (2-ethyl hexyl) phthalate (DEHP). In addition, 2-ethyl-hexanol was used as solvents, oils and additives, paint and coating additives, fuel and fuel additives, agricultural chemicals (non-pesticides), and intermediates. Until now, 2-ethyl-hexanol was produced in the industry through oxo process with synthesis gas and propylene as raw materias [1]. One of the steps in the oxo process was a consecutive hydrogenation of the 2-ethyl-2-hexenal to 2-ethyl-hexanol via the 2-Ethyl-hexanal or 2-ethyl -2-hexenal as intermediate products. The objective of this research was to get the kinetics model of 2-ethyl-2-hexenal hydrogenation on the best nickel based catalyst, which gives the high selectivity to 2-ethyl-hexanol.

2. Experimental
2.1. Catalyst synthesis
The hydrogenation catalyst consisted of two components, namely Nickel (Ni) active metal as the active phase (main component) and support (γ-alumina and cab-o-sil). As a metal source, Ni was selected by nitrate salt solution. The support was in the form of a mixture of alumina and silica synthesized from AIP2 (Indonesian Patent No: P00201701287 - granted) and cab-o-sil. The catalyst
was synthesized by peptization method with 50 % nickel content and the composition of silica in the support was varied, that was 0 % (NiO50-Cab0), 20 % (NiO50-Cab20), 50 % (NiO50-Cab50), 80 % (NiO50-Cab80), and 100 % (NiO50-Cab100).

2.2. Characterization of catalyst

The physical properties of the catalyst, namely surface area, average pore diameter, and average pore volume were measured using the surface area with BET method and the pore size analyzer of the Quantachrome brand NOVA 320E type with the BET method. The hydrogen chemisorption profile was measured using Chem-BET Pulsar TPR/TPD (Temperature Programmed Reduction/Desorption). Identification of compounds of catalysts were measured using Bruker D8 Advance X-ray diffractometer with Cu anode. Analysis of the composition of the reaction mixture produced using a GC (gas chromatography) equipment type Shimadzu 2010 plus a type of column RTX-5, Flame Ionization Detector, and helium as carrier gas.

2.3. Catalyst activity test

The 2-ethyl-2-hexenal hydrogenation reaction was carried out in an isothermal fixed bed reactor at a temperature of 100-120°C, a pressure of 30 bar. Feed in the form of a mixture of 2-ethyl-2-hexenal and 2-ethyl hexanol with a ratio of 1:4 flowed into the reactor at a rate to provide a LHSV (Liquid Hourly Space Velocity) of 1-1.75 hours\(^{-1}\). Hydrogen gas flowed at a rate of 30 ml/min. Previously the catalyst activation was carried out in situ using a gas with a flow rate of 30 ml/min, 500°C and a pressure of 3-7 bar for 3 hours. The reactor system setup was presented in Figure 1.

**Figure 1.** Set up a continuous reactor system
2.4. Kinetics Data Processing
The data obtained was processed using Microsoft Excel and MATLAB soft frames. The parameter values of the rank power law kinetics model were the reaction order, activation energy ($E_a$) and Arrhenius constant ($k_0$).

3. Results and Discussion
3.1. Characterization and activity test of catalysts
3.1.1. X-Ray Diffraction method results.
Analysis with the X-Ray Diffraction (XRD) method was used to determine the types of crystals contained in the synthesized catalyst. The diffractogram in Figure 2a showed several forms of the constituent crystal structure of the catalyst in the range of $2\theta$ from 0° to 100°. X-Ray diffractogram catalyst compared with standard data available in JCPDS (Join Committee on Powder Diffraction Standards). From Figure 2a, there was 3 main peaks at diffraction angles ($2\theta$) 37.13°, 43.18° and 62.78°, 75.33°, 79.32°, 95.02° which all show the form of NiO crystals (111), (200), (220), (311), (222), and (400). The diffractogram on the NiO50-Cab50 catalyst was not too different from the NiO diffractogram and did not indicate the peak of the SiO$_2$ and Al$_2$O$_3$ support crystals, probably because the support was completely mixed with NiO when preparing. In addition, sharp NiO crystal peaks can be caused by the occurrence of NiO agglomerations forming larger crystals due to the high temperatures used when calcination [2].

3.1.2. TPR method results.
Analysis of the Temperature Programmed Reduction (TPR) method was used to determine the reduction temperature of the synthesized catalyst. The TPR profile (Figure 2b) on the NiO50-Cab0 catalyst showed the two highest reduction temperature peaks, namely 480°C and 608°C while the NiO50-Cab50 catalyst showed the lowest reduction temperature of 450°C and 520°C. This can be caused by the interaction between NiO and Al$_2$O$_3$ which strongly form NiAl$_2$O$_4$ which was difficult to reduce, thus requiring a higher reduction temperature while the interaction between NiO and SiO$_2$ was weaker, so it was more easily reduced at lower temperatures.

![Figure 2](image-url) Results of characterization with the (a) XRD method and (b) TPR method

The peak that appeared on the catalyst with cab-o-sil composition higher or equal to 50 had only one reduction peak, while the catalyst with cab-o-sil composition lower than 50% has more than one reduction peak. The peaks showed different species from NiO: the range 250-350°C showed the
crystalline segregation form which had very weak interaction with the support, the range 350-500°C showed NiO which binded to the support, the range 500-750°C showed NiO which was strongly bounded to Al2O3 forms nickel aluminate (NiAl2O4). Species with very strong bonds between NiO and supports were shown at a higher reduction temperature because it was difficult.

3.1.3. BET method results.

Analysis with the BET method was carried out using Quantachrome NOVA’s 3200E Surface Area Analyzer by using nitrogen as adsorbate. The results of catalyst analysis with the BET method were shown in Table 1. Characterization results on the catalyst sample indicate that the largest catalyst surface area was NiO50-Cab0. According to Gobara and Hassan [3], the catalyst with SiO2 support produces the largest catalyst surface area. However, the phenomenon on catalysts with cab-o-sil which was getting higher shows the opposite result. The surface area of the synthesized catalyst with a larger SiO2 support (higher cab-o-sil), did not produce a larger surface area. Probably, this was due to nickel metal sintering in SiO2-supported catalysts due to weak Si-Ni interactions [4]. The weak Ni-Si interaction was supported by TPR data which shows the reduction temperature of the NiO50-Cab100 catalyst was lower, so it can be concluded that the interaction was easier to reduce at a lower temperature than the NiO50-Cab0 catalyst which had a higher reduction temperature.

Table 1 The physical properies of catalyst (using the BET method)

| No. | Catalyst          | Surface Area (m²/g) | Pore Volume (cc/g) | Pore Size (Å) |
|-----|------------------|---------------------|-------------------|---------------|
| 1   | NiO50-Cab0       | 188.873             | 0.22697           | 42.785        |
| 2   | NiO50-Cab20      | 117.153             | 0.21794           | 37.206        |
| 3   | NiO50-Cab50      | 106.870             | 0.25144           | 47.055        |
| 4   | NiO50-Cab80      | 103.371             | 0.23373           | 45.222        |
| 5   | NiO50-Cab100     | 117.510             | 0.24238           | 41.253        |

In the NiO50-Cab80 catalyst, the SiO2 content was greater than that of Al2O3, resulting in more nickel metal deposited in SiO2 while a weak Ni-Si bond was easily sintered at the time of reduction. This caused a decreased surface area and a larger pore size. Meanwhile, on the NiO50-Cab20 catalyst, the Al2O3 content was greater than SiO2, producing more nickel metal deposited in Al2O3. The large surface area affected by the stronger Ni-Al bond was not easily subjected to sintering at the reduction temperature used.

3.1.4 Activity test results

In the activity test in a fixed bed reactor, the conversion data and selectivity were taken when the reaction reaches a steady state. The 2-ethyl-2-hexenal hydrogenation reaction was a consecutive reaction with intermediate products in the form of 2-ethyl-hexanal and 2-ethyl-hexanol final products. Although catalyst conversion was one indicator of catalyst activity, this indicator cannot measure how efficiently the catalyst worked. The performance of the catalyst also depends on selectivity. High selectivity allows few side reactions, so the acquisition of the main product becomes high.

Large pore size was thought to affect the value of selectivity. Based on the BET results, the NiO50-Cab50 catalyst showed the largest pore volume between synthesized catalysts that had the highest selectivity value. Consecutive selectivity values from the largest to smaller values: NiO50-Cab50 > NiO50-Cab100 > NiO50-Cab80 > NiO50-Cab0 > NiO50-Cab20 (Table 2). This sequence also applies to the pore volume measured by the BET method (Table 1).
Table 2 Performance of catalysts at 120 °C, 30 bar, LHSV 1 hour⁻¹

| No. | Catalyst        | Conversion, X (%) | Selectivity, S (%) |
|-----|-----------------|-------------------|-------------------|
| 1   | NiO50-Cab20     | 98.73             | 16.09             |
| 2   | NiO50-Cab50     | 98.29             | 87.41             |
| 3   | NiO50-Cab80     | 73.46             | 56.34             |
| 4   | NiO50-Cab100    | 96.02             | 66.10             |

3.2. The Kinetics Model
3.2.1 Internal Diffusion Limitation
The pore diffusion significance can be seen from the Thiele Modulus (Φ) and effectiveness (η). Thiele modulus describes a decrease in the concentration of reactants in the pore of the catalyst [5]

\[
\Phi^2 = \frac{k_1 R^2 S_a \rho_p C_{AS}^{2-1}}{D_e}
\]  

With \( k_1 \) being the reaction rate constant, \( R \) was the catalyst radius, \( S_a \) was the catalyst specific surface area, \( \rho_p \) was the catalyst density, \( C_{AS} \) was the concentration on the catalyst surface \((mol/m^2)\), and \( D_e \) was the effective diffusivity in the liquid phase. From the calculation of the Thiele Modulus using equation (1), the value of \( \Phi \) was 1.387. In this study, the value of the small value of the Thiele Modulus showed the rate of pore diffusion was fast and not as determining stage of reaction. The concentration profile in the catalyst pore, can be calculated by equation (2) and by equation (3) using FlexPDE.

\[
\frac{d^2 \varphi}{d \lambda^2} + \frac{2}{\lambda} \frac{d\varphi}{d \lambda} - \Phi^2 \varphi = 0
\]  

\[
\varphi = \frac{C_A}{C_{AS}} ; \quad \lambda = \frac{r}{R}
\]  

Figure 3 showed the distribution of reactant concentrations from the catalyst surface \((r = R)\) to the center of the catalyst \((r = 0)\) at various values \( \Phi \). The value of \( \Phi \) 1.387 occurs only in all parts of the catalyst pore and the reaction reaches the center of the catalyst so that all parts of the catalyst were utilized. This showed that mass transfer in pores was fast and the reaction was not influenced or controlled by internal diffusion so that the study of catalyst kinetics was in a kinetic regime.
3.2.2 Determination of Kinetics Parameter

The 2-ethyl-2-hexenal hydrogenation reaction product was identified through GC method analysis. The results of the analysis in the form of chromatograms showed the peaks that appear at certain retention times according to the type of compound at the retention time. Identification was known based on previous research literature data through testing using a standard solution made from a mixture of t-butanal, i-butanal, n-butanal, i-butanol, n-butanol, 2-ethyl-2-hexenal and 2-ethyl-hexanol. The hydrogenation of 2-ethyl-2-hexenal products identified through the GC method analysis are 2-ethyl-hexanal and 2-ethyl-hexanol. The 2-ethyl-hexanal products were known as intermediate products. The 2-ethyl-hexanol product was formed because of the hydrogenation reaction of the C = C double bond in 2-ethyl-2-hexenal.

The hydrogenation 2-ethyl-2-hexenal consecutive reaction rate equation was shown in Equations 4-6:

\[ r_{en} = -k_1 \cdot C_{en}^m \]  
\[ r_{an} = k_1 \cdot C_{en}^m - k_2 \cdot C_{an}^n \]  
\[ r_{an} = k_2 \cdot C_{an}^n \]

Optimization of kinetic parameters was done in order m, n, k₁, and k₂ values. Optimization was done by matching the data with a model that provided minimal FOBJ (objective function) values. The results of the optimization of the hydrogenation reaction at 120°C, 30 bar, obtained the value of m and n was 1 and the values of k₁ and k₂ are 1.9866 and 3.9498 (mol.L.hr⁻¹) respectively. Distribution of experimental data and optimization results by modeling using MATLAB (Figure 5) according to the mechanism of consecutive reactions in the proposed hydrogenation of 2-ethyl-2-hexenal as Figure 4.

Meanwhile, the determination of reaction kinetics parameters to get the activation energy value (Eₐ) and Arrhenius constant (k₀) in the 2-ethyl-2-hexenal hydrogenation reaction calculated using Microsoft Excel followed the rank law model using Equations 3-5 at various temperature variations (100-120°C). Experimental data curves on various temperature variations were shown in Figure 5. Data processing methods were performed by distributing ln k₁ and ln k₂ values to 1/T as Equation 7 and the results of the calculations were summarized in Table 3.

\[ \ln k_1 = \ln k_0 - \left( \frac{E_a}{R \cdot g} \right) \frac{1}{T} \]

Figure 4 Hydrogenation 2-ethyl-2-hexenal pathway to 2-ethyl-hexanol [6]
Table 3  Kinetics parameter of hydrogenated 2-ethyl-2-hexenal consecutive reactions on NiO50-Cab50

| No. | Reaction                                      | Activation energy | Arrhenius contant |
|-----|-----------------------------------------------|-------------------|-------------------|
| 1   | 2-ethyl-2-hexenal +H₂→ 2-ethyl-hexanal      | $E_a = 33.66$ kJ/mol | $k_{01} = 2.19 \times 10^4$ |
| 2   | 2-ethyl-hexanal + H₂→ 2-ethyl-hexanol        | $E_a = 58.39$ kJ/mol | $k_{02} = 1.70 \times 10^5$ |

Figure 5 (a) Product and reactant concentration (en =2-ethyl-2-hexenal; an = 2-ethyl-hexanal; on = 2-ethyl-hexanol) in 2-ethyl-2-hexenal hydrogenation reaction at 120 °C and 30 bar using NiO50-Cab50 catalyst (b) profile of 2-ethyl-2-hexenal concentration at various temperatures (100 -120°C).

The low value of activity energy showthat the reaction increases rapidly with increasing temperature. The values of $E_a_2 > E_a_1$ showed that the hydrogenation reaction in the C = C double bond to form 2-ethyl-hexanal was easier than hydrogenation in the C = O double bond to form 2-ethyl-hexanol. This mechanism illustrates that there was competition between 2-ethyl-2-hexenal and 2-ethyl-hexanal in occupying the active side of the catalyst [7].

4. Conclusions
The conclusion obtained from this research was the rate of reaction obtained from this experiment was not influenced by internal diffusion so that the equation obtained was the kinetics equation. NiO50-Cab50 catalyst converts 2-ethyl-2-hexenal to 2-ethyl-hexanal faster than converting 2-ethyl-hexanal to 2-ethyl-hexanol.

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