

Effect of molybdenum addition in nickel-based catalyst on hydrogenation reaction of 2-ethyl-2-hexenal hydrogenation to 2-ethyl-hexanol

Stephanie Virgana *, Harry Hans J., Iyan Wanadi G., Melia Laniwati G, Subagjo, IGBN Makertihartha

Department of Chemical Engineering, Faculty of Industrial Technology Institut Teknologi Bandung, Ganesa 10, Bandung, 40132, Indonesia

*Corresponding author E-mail: stephanie.virgana@students.itb.ac.id

Abstract

The 2-ethyl-hexanol compound is 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. One of the steps in the oxo reaction is consecutive hydrogenation reaction of the 2-ethyl-2-hexenal to 2-ethyl-hexanol. This reaction requires nickel-based catalyst as an effective step for obtaining higher and purer 2-ethyl-hexanol yields. This research aims to develop the formula and procedure of catalyst synthesized in Laboratory of Catalysis and Reaction Engineering Institut Teknologi Bandung and get a rate of the reaction. The catalysts were synthesized by co-impregnation with a nickel content of 20%-w and varied with molybdenum loading (5-20%). The support that used for these metals is alumina-phosphate (AIP2). The synthesized catalysts were tested for their activity against the 2-ethyl-2-hexenal conversion at 120°C, 30 bar in the fixed bed reactor and compared its performance with a commercial catalyst. The results showed the addition of molybdenum loading increases selectivity of 2-ethyl-hexanol but decrease the conversion of 2-ethyl-2-hexenal. The highest selectivity was achieved by Ni5-Mo20/AIP2 (X=31%, S=85%), but the highest conversion was achieved by Ni20/AIP2 (X=88%, S=32%). Nickel tend to play a part of breaking the C=C bond. Meanwhile, molybdenum tends to break the C=O bond. This shows that the hydrogenation of C = C bonds and the C = O bond is very depending on nickel and molybdenum metal loading.

Keywords: 2-Ethyl-Hexanol; Nickel Catalyst; Hydrogenation.

1. Introduction

The 2-ethyl-hexanol compound is much needed in the plasticizer industry as a precursor for the synthesis of bus diesters (2-ethyl hexyl) phthalate (DEHP). In addition, 2-ethyl-hexanol is commonly used as solvents, lubricants and lubricant additives, paint and coating additives, fuel and fuel additives, agricultural chemicals (non-pesticides), and intermediates. Generally, 2-ethyl-hexanol is produced in the industry through oxo reactions (Agency, 2006; Both et al., 2009 and 2013).

Indonesia also produces 2-ethyl-hexanol compounds through oxo reaction. One of the steps in the oxo reaction is the 2-ethyl-2-hexenal hydrogenation reaction to 2-ethyl-hexanol. This reaction requires a nickel-based catalyst as the most effective step for obtaining a higher and purer 2-ethyl-hexanol recovery. In the absence of a catalyst, the hydrogenation reaction proceeds very slowly and can be accelerated by very high-temperature conditions. The need for hydrogenation catalyst in Indonesia reaches 100 tons per two years. The need for such catalysts is still met by means of imports, thus causing dependence on foreign parties. Therefore, the Chemical Reaction and Catalysis Reaction Laboratory (CARE) Bandung Institute of Technology conducted a study on the synthesis of the nickel-based 2-ethyl-2-hexenal hydrogenation catalyst to prepare itself to become an independent nation in meeting the needs of the catalyst.

2. Experimental

2.1. Materials

The hydrogenation catalyst comprises two components, Ni active metal as the active phase (main component) and support (γ -alumina, AIP2). As a source of Ni metal, nitrate salt solution of Ni ($\text{Ni}(\text{NO}_3)_2$) and a molybdenum salt of $\text{Na}_2\text{MoO}_4 \cdot 7\text{H}_2\text{O}$ was obtained. The alumina phosphate support used is a modified alumina phosphate support 2% (AIP2) that has been available at Chemical Reaction Engineering Laboratory and Catalysis Institute of Technology Bandung. The catalytic activity test of the hydrogenation process using a liquid feed in the form of a 2-ethyl-2-hexenal and 2-ethyl-hexanol mixture. For gas chromatography analysis using hydrogen gas, helium, and nitrogen produced by IGI / BOC, Jakarta.

3. Characterization

3.1. Fixed-bed reactor

Test of catalyst activity using fixed bed reactor. The catalyst used for each activity test is 1 g of weight with feed flow rate of 1 ml/min total. The feed consisted of a 2-ethyl-2-hexenal and 2-ethyl-hexanol

mixture with a weight ratio of 1: 4. The image of the reactor circuit is shown in Figure 1.

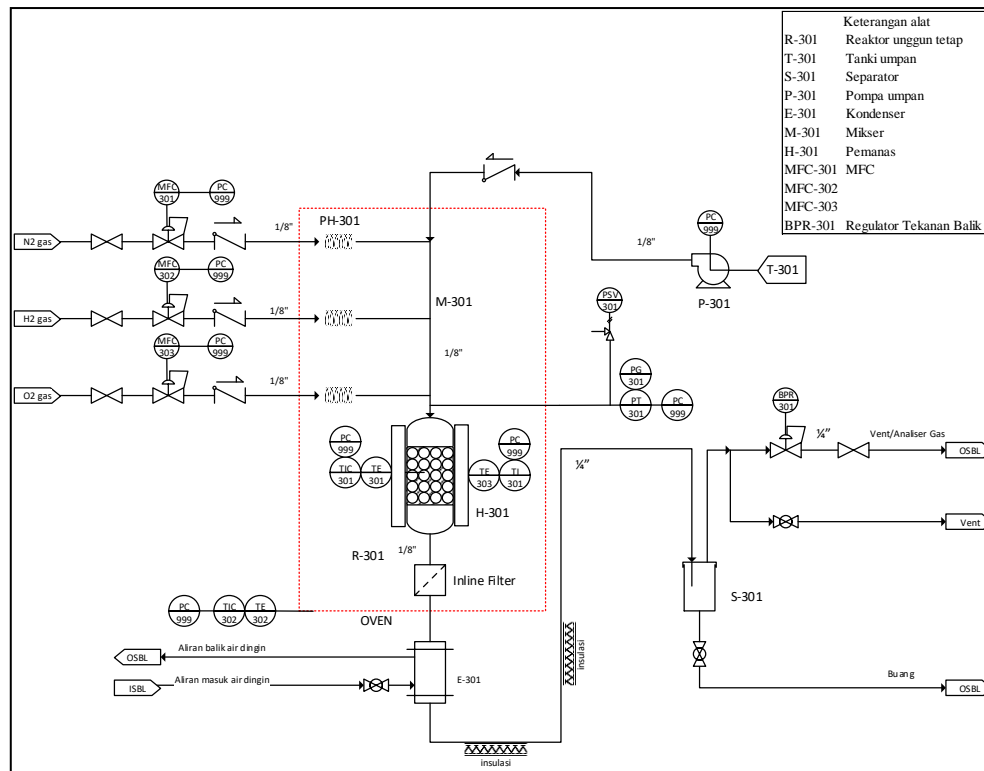


Fig. 1: Fixed-Bed Reactor Scheme.

3.2. Gas chromatography

The analysis of the composition of the reaction mixture was generated using a set of Shimadzu 2010 type GC (gas chromatography) equipment plus RTX-5 column type, FID detector, and helium and hydrogen carrier gas.

$$Xen_i(\%) = \frac{C_{en0} - C_{eni}}{C_{en0}} \times 100\%$$

$$Son_i(\%) = \frac{C_{oni} - C_{on0}}{C_{en0} - C_{eni}} \times 100\%$$

$$San_i(\%) = Son_i(\%) \times Xen_i(\%)$$

were X_{en} being percentage of conversion of 2-ethyl-2-hexenal, S_{on} being percentage of selectivity of 2-ethyl-hexenol, and S_{an} being percentage of selectivity of 2-ethyl-hexanal. C is the concentration for 2-ethyl-2-hexenal (C_{en}), 2-ethyl-hexenol (C_{an}), and 2-ethyl-hexanol (C_{on}). C_0 for initial concentration and C_i for hourly concentration.

4. Results and discussion

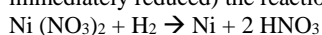
4.1. Activity test catalyst

Activity test conducted for 6 hours. the conversion and selectivity of the catalysts are calculated when the condition reaches steady state.

Table 1: Summary Test Results of Catalyst Activity

No	Support	Name of Catalyst	Composition		Temperature	Xen (%)	Son (%)
			Ni (%-b)	Mo (%-b)			
1	AIP2	Ni20-AIP2-SK	20	-	Tcal=550°C, Tred=400°C	35,09	86,44
2		Ni20-AIP2-K	20	-	Tcal=400°C, Tred=600°C	75,15	36,74
3		Ni20-AIP2-TK	20	-	without calcination, Tred=600°C	82,95	23,34
4		Ni15Mo3-AIP2-K	15	3	Tcal=400°C, Tred=500°C	77,47	48,67
5	γ -alumina	Ni20Mo5-AIP2-K	20	5	Tcal=400°C, Tred=500°C	77,71	47,88
6		Ni20-Gama-K	20	-	Tcal=400°C, Tred=600°C	13,82	5,05
7		Ni5Mo20-Gama-K	5	20	Tcal=400°C, Tred=600°C	11,69	14,12
8		Ni3Mo15-Gama-K	3	15	Tcal=400°C, Tred=400°C	19,32	-76,27

The results of the activity test on Ni20-AIP2-K catalyst (calcined) compared with Ni20-AIP2-TK (without calcination), the result of conversion and selectivity are not much different. This shows that the calcination process does not significantly affect the nickel impregnation catalyst in the AIP2 support. A high reduction temperature (600°C) can reduce the $NiAl_2O_4$ species to a nickel metal form formed from the calcination process (Yang et al., 2009). However, in subsequent experiments, the calcination process was carried out, since without the calcination process (after drying, the catalyst was immediately reduced) the reaction proceeded as follows:



The resulting nitric acid feared could damage the reactor because of its acidic nature, so calcination is still needed.

The excessively high calcination temperature at the time of catalyst synthesis can decrease the catalyst activity. This may be due to; high calcination temperatures result in the formation of the difficulty-reducible $NiAl_2O_4$ species and the inactive 2-ethyl-2-hexenal hydrogenation.

On a larger nickel composition than the molybdenum composition with an AIP2 catalyst support, the conversion and selectivity are not significantly different. While, for all catalyst variations using γ -alumina, the resulting conversion and selectivity are low. In addition,

the greater molybdenum content of the nickel content in the catalyst will direct the catalyst to form an intermediate (2-ethyl-hexanal) product and this is undesirable. These areas need improvement in both selectivity and activity; the selection of the co-catalyst, the modification of the ligands, and the reaction conditions are all controllable and essential features of such systems.

5. Conclusion

The addition of molybdenum improves selectivity but decreases the activity of the catalyst. The performance of the catalyst is greatly determined by the calcination and reduction temperature used during catalyst synthesis. In addition, different support types also show differences in conversion value and catalyst selectivity.

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