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PREPARATION, CHARACTERIZATION, AND CATALYTIC ACTIVITY TEST OF Ni-Mo/NATURAL ZEOLITE ON PYRIDINE HYDRODENITROGENATION

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ABSTRACT

Preparation, characterization, and catalytic activity test of Ni-Mo/natural zeolite on pyridine hydrodenitrogenation were carried out. Preparation of catalyst was conducted by impregnation method using nickel nitrate hexahydrate and ammonium heptamolibdate precursor as Ni and Mo source respectively. Characterization of catalyst was conducted by using gravimetry, atomic absorption spectrophotometry, and X-ray diffraction method. Catalytic activity test on pyridine hydrodenitrogenation was carried out by using flow system reactor with hydrogen flow rate variable. The research results showed that the catalyst's total acidity and crystallinity are increased with level of impregnation success of 96.71% and 90.08% respectively. Ni-Mo/natural zeolites able to increase the catalytic conversion up to 71.78% at 350 °C and hydrogen flow rate of 10 mL/min with more highly varied product distribution. Assuming that the pyridine hydrodenitrogenation follows the pseudo first order kinetics.

Keywords: *hydrodenitrogenation, pyridine, Ni-Mo/natural zeolite*

INTRODUCTION

Petroleum quality from year to year markedly decreases with the increasing content of nitrogen, sulfur, oxygen, halogens, and metals. So it could be ascertained that the content of them in the petroleum fractions have been increased. For that, it needs the hydrotreating processes including the hidrodenitrogenation (HDN) process of heavy fractions in order to remove the nitrogen contents in them so that they can be processed further into lighter fractions.

HDN reaction can be accelerated by the catalyst. Research for designing catalysts with the activity, selectivity, and high stability constant basis. The catalysts used in HDN process are modified Ni-Mo bimetallic catalysts [1,7,10-12]. Ni-Mo bimetallic catalysts have been widely known as a commercial catalyst which has the high activity, selectivity, and stability. To improve their performance, Ni-Mo bimetallic catalysts are impregnated on the various supports such as NaY-zeolite [1], Al_2O_3 [2,18], pillared-clay [8], ZrO_2–Cr_2O_3 [13], and carbon nanotubes [4]. Recently, one of the supports that is often used as a metal support catalysts is natural zeolite. Utilization of natural zeolite as a support should be developed because, it has a high surface area, chemical, and hydrothermal stability. Natural zeolite also has an adjustable pore size, hydrophilicity, and acidity. These properties are supported by a high level of dispersion, capability of stabilizing metals and forming a bifunctional catalyst, and can be made in various desired shapes.

Impregnation of Ni-Mo on the natural zeolite is expected to improve the performance of Ni-Mo catalysts in the HDN reaction. Furthermore, the design of Ni-Mo/natural zeolite catalyst should be followed by the determination of an appropriate reaction parameters. Base on the above explanation, the authors undertaken the research of preparation, characterization, and catalytic activity test of Ni-Mo/natural zeolite on pyridine hydrodenitrogenation.

Pyridine HDN reaction was conducted in a flow reactor system. All components passing through the reactor with the same flow rate would have the same contact time. Kinetics of pyridine HDN catalyzed by Ni-Mo/natural zeolite was assumed that the pyridine HDN on the catalyst surface reaction kinetics followed the pseudo first order.

The rate of pyridine HDN has been measured in a flow reactor system with a constant broad cross section, the given reactant flow rate *u* over a constant bulk catalyst volume d*V*, where the concentration of an element coming into the unit *i* is c_i, and the concentration of the leaving unit is c_i + dc_i, so the approach for the kinetics of the reaction rate r_i can be expressed as follows:

$$\frac{dn_i}{dt} = r_i dV - u dc_i \quad (1)$$

Assuming that the reaction occurs in a steady state and the reaction takes place in a closed system,

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the measurement of pyridine HDN reaction rate with Ni-Mo/natural zeolite catalysts using a flow reactor at a given time t can be done by using the equation as follow:

$$k = \frac{u}{V} \ln \frac{c_0}{c} \tag{2}$$

where rate constant k is the reduced pyridine, μ is the reactant flow rate (mL/min), V is the volume of bulk catalyst (mL), c and c_0 are respectively the concentration of reactant when exiting the reactor and concentration when entering the reactor, so that u/V can replace the t variable [3].

EXPERIMENTAL SECTION

Materials

This work consists of two main steps, they are preparation of catalyst and its activity test. Materials used in this preparation step were natural zeolite (PT. Prima Zeolita Yogyakarta) as support of active metals, aquabidest (Chemistry Lab.) for all solvation process, ammonium heptamolibdate $(NH_4)_6Mo_7O_{24}.4H_2O$ (E. Merck) and nickel(II) nitrate hexahydrate $Ni(NO_3)_2.6H_2O$ (E. Merck) as Ni and Mo sources respectively. Hydrochloric acid HCl 37% (E. Merck) and ammonium chloride NH_4Cl (E. Merck) were used in acid treatment in order to dealuminate and convert natural zeolite into H-natural zeolite, respectively. Nitrogen, oxygen, and hydrogen (PT. Samator Gas) were used in the calcination, oxidation, and reduction process, respectively. In order to determine the total acidity of prepared catalyst by the gravimetric method, NH_3 25% was used as adsorbate. Pyridine 99.5% (E. Merck) was used as feed on activity test of catalyst.

Instrumentation

In the preparation step, 1 set of reflux, vacuum pump, oven Precision GCA Corp., analytical balance AND GR-200, porcelain crucible, sieve of 100 mesh, desiccator, calcination and / or reduction reactor, electric heater, 1 set of Buchner filter, and several equipments and glassware were used. In the characterization steps, AAS Perkin Elmer Aanalyst-100, FT-IR Shimadzu, and X-Ray Diffractometer Philips type X'pert were used, beside of flowable desiccators. HDN reactor, furnace type 21100, thermometer, regulator Matsunaga, flowmeter influx Caché, and product containers were used in the activity test step. The product was analyzed by using GC HEWLET PACARD 5890 series II and GC-MS SHIMADZU QP-2010S.

Procedure

Preparation and characterization of Ni-Mo/natural zeolite catalyst

Precursor ammonium heptamolibdate $(NH_4)_6Mo_7O_{24}.4H_2O$ and nickel(II) nitrate hexahydrate $Ni(NO_3)_2.6H_2O$ solution of 2:1 in weight ratio of Ni:Mo, in which the weight of metals were 1% of the weight of zeolite were prepared. Natural zeolite was dipped in $Ni(NO_3)_2.6H_2O$ solution so that entirely submerged. Mixture stirred slowly at room temperature for 12 h, then filtered and dried in an oven at ±110 °C, then weighed until constant. Impregnation had returned for a second metal $(NH_4)_6Mo_7O_{24}.4H_2O$ solution by the same method so that resulting the Ni-Mo/natural zeolite catalyst [14]. Catalysts obtained then were calcined by flowing nitrogen, oxidized by oxygen, and reduced by hydrogen gasses. Characterizations of catalysts including acidity test, determination of crystallinity, and metal content were carried out respectively by using NH_3 and pyridine adsorption, XRD, and AAS.

Study on effect of hydrogen flow rate

One gram of catalyst was inserted into the column reactor, subsequently inserted into the furnace reactor. Pyridine as the feed was inserted into the boiling flask and connected to the reactor column. Boiling flask was then connected with hydrogen gas. Furnace was heated to a temperature of 350 °C. Hydrogen gas flow rate was set 10 mL/min and feed vaporized and fed to a reactor. Product formed is passed through a cooling spiral that had been linked with a mixture of ice and salt. Products were collected for 60 min. Products were taken and put into a container product. The same step was repeated with variations of the hydrogen flow rate of 20, 30, and 40 mL/min with a catalyst that had been replaced. Products collected were analyzed using GC and GC-MS.

RESULT AND DISCUSSION

Preparation of Ni-Mo/Natural Zeolite Catalyst

Preparation of Ni-Mo/natural zeolite catalyst was conducted by impregnation method using precursor solution of Ni(II) nitrate hexahydrate and ammonium heptamolibdate impregnated alternately. The total mass of impregnated metals was 1% of natural zeolite. Impregnation process has been carried out during 12 h in the hope that all metals have been impregnated. After impregnation process, the catalyst was dried in

Table 1. Catalyst's acidity by gravimetry method

Solid catalyst	Number of acid sites (mmol ammonia/g)	Number of acid sites (mmol pyridine/g)
H-natural zeolite	4.34	0.97
Ni-Mo/natural zeolite	6.00	1.50

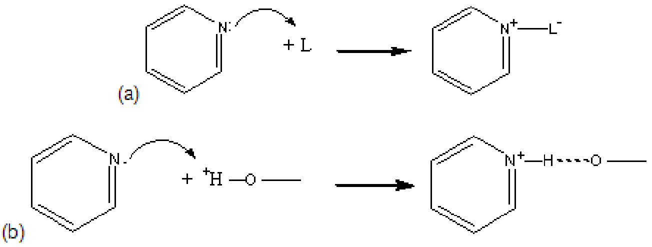

Fig 1. Interaction of pyridine (a) on metal surface as a Lewis acid site, and (b) proton as a Brønsted acid site

order to lower water contents so that the catalysts can be pulverized into fine granules by a mechanical process. Calcination process has been done so that more equitable distribution of metals. It causes the Si/Al ratio on the surface is higher than the bulk which results in increased acidity of the catalyst.

Oxidation process had been carried out so that the impregnated elements were converted to oxides so that the non-metallic elements that are not expected to be impregnated can be released [5].

$$Ni_3Mo_7O_{24}.xNH_3(s)+2.5xO_2(g)\rightarrow 3NiO(s)+7MoO_3(s)+xNO_2(g)+1.5xH_2O(g)$$

The NO_2 gas and water vapor will be carried and released with the flow of gas. Reduction process has been performed to convert metal oxides into metal [5].

$$NiO(s) + H_2(g) \rightarrow Ni(s) + H_2O(g)$$

$$MoO_3 + 3H_2(g) \rightarrow Mo(s) + 3H_2O(g)$$

Characterization of Ni-Mo/Natural Zeolite Catalyst

Acidity test of Ni-Mo/natural zeolite catalyst

Acidity test was conducted by ammonia and pyridine adsorption. Ammonia and pyridine were chosen as adsorbates because they are small molecules allowing them to be adsorbed not only on the surface but also in the zeolite channels. In addition, ammonia can also act as Lewis and Brønsted bases so that the total acidity can be determined well. Determination of acidity of the catalyst with pyridine used to determine the Lewis acid sites only, because pyridine can only act as a Lewis acid alone. The results of acidity test of zeolite and Ni-Mo/ natural zeolite with ammonia and pyridine adsorption are presented in Table 1.

Table 1 shows that the acidity of natural Ni-Mo/zeolite higher than the H-zeolite, which means that the impregnation of Ni-Mo metals in the natural zeolite increases the acidity of both the total acidity as well as Brønsted acid sites of catalyst. This can be understood by considering that Ni and Mo metals are transition metals with d-orbital, which have the ability to form complexes with ammonia and pyridine ligands. So the metal acts as a Lewis acid (lone pair electron acceptors). Binding of ammonia or pyridine by transition metals is much greater than the natural zeolite acid sites for each metal can bind at least two molecules of ammonia or pyridine.

Acid character of the metal is a Lewis acid character, so that the addition of bimetallic Ni-Mo will increase the ratio of Lewis acid sites that play an important role in initiating pyridine sticking on catalyst. Delivery of the electron pair of N to metal clusters or delivery of protons by the Brønsted acid sites can initiate HDN reaction because both can reduce the electron density around the N atom so that becomes more positively charged thus decreasing ring's aromaticity (Fig. 1). Because the Brønsted acid-base interaction is weaker than of Lewis acid-base, then pyridine activated by a Lewis acid is more reactive. Besides of the distance of pyridine from the catalyst's surface is also shorter so it is more possible for the occurrence of HDN products on Lewis acid sites than the Brønsted acid sites.

Impregnated metal contents

The impregnated metal contents have been determined by using atomic absorption spectroscopy (AAS). The results showed that Ni and Mo contents in natural zeolite respectively are 6447.67 ppm and 3002.8 ppm. Based on theoretical calculations of impregnated-Ni and -Mo contents are respectively 3333.3 ppm and 6666.7 ppm, which means the level of success with this impregnation method for Ni and Mo are respectively 96.71% and 90.08%. In the impregnation process, Ni was impregnated before Mo, so there is no competition of counterions. Theoretically, if it is studied from the metal content of salts, impregnation was undergone perfectly if only if the Ni/Mo ratio is 2. The test result showed that the ratio of Ni/Mo was 2.15. It can be seen that the ratio of Ni/Mo impregnation results are slightly higher than the theoretical one if the study from the metal content of the salts is considered. In this case, the ratio of Ni/Mo in each salt solution is not the only one factor determining of ratio of impregnated Ni/Mo. There are other factors that determine the ratio of impregnated Ni/Mo, namely the amount of Ni (II)-hepta molybdate formed the zeolite pore size, and the size of the metal

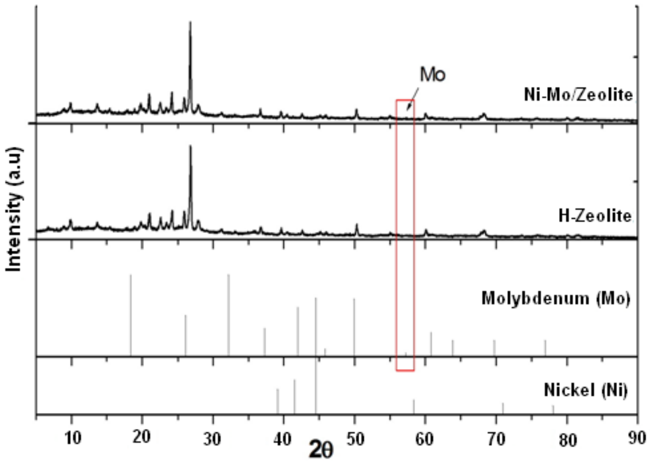

Fig 2. XRD patterns of (a) natural zeolite and (b) Ni-Mo/natural zeolite

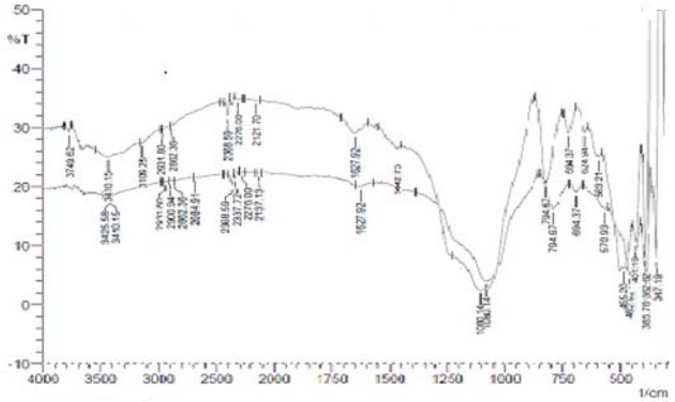

Fig 3. FTIR spectra of (a) H-natural zeolite and (b) Ni-Mo/natural zeolite

cation or anion of impregnated metals. Molybdate anion is a bulky anion which is relatively more difficult to be impregnated to surface of zeolite than Ni cations, besides Mo only can be impregnated through adsorption method, while Ni occurs via cation exchange and adsorption methods.

It was found that the catalyst prepared by sequential impregnation of NiO and MoO_3 was more active [1] than the catalyst prepared by coimpregnation. Among the sequentially impregnated catalysts, the catalyst in which NiO deposited first followed by MoO_3 shows high HDN activity. TEM, FT-IR spectra of CO adsorption, and estimation of total sulfur of sulfide catalyst results clearly show that the NiO and MoO_3 are well dispersed over support on reverse order impregnated catalyst. The very low activity of coimpregnated catalyst is attributed to poor dispersion of metal oxides as well as due to the formation of stable stoichiometric oxide and aggregates of metal particle over the support surface.

Crystallinity of catalyst

To determine the crystallinity of catalyst, examination by XRD was conducted. The result can be shown by Fig. 2. Based on Fig. 2, it is generally seen that the base line of diffractogram of H-natural zeolite is still widening, especially in the range of 0.0-30 degrees, while for Ni-Mo/zeolite more subtle. This shows that in general the crystallinity of Ni-Mo/natural zeolite is higher than natural zeolite, which means that the impregnation of metals can increase the crystallinity of zeolite. Ni and Mo as active metals have a tendency to form crystalline structures, while non-metallic elements tend to form an amorphous structure. So the replacement of elements of H-zeolite with bimetals Ni-Mo can absolutely increase the crystallinity of zeolite.

Form Fig. 2 also can be seen the existence of the intensity shift between first and second peak before and after impregnation. Third peak of Ni-Mo/zeolite has a different appearance of 2θ from H-zeolites. This is attributable to the strengthening of the intensity at 2θ = 6.419° as a result of interference with signals of Ni-Mo. Whereas the FWHM of the corresponding main peak did not differ significantly. It means that the crystal size does not change significantly.

On diffractogram of Ni-Mo/natural zeolite, the peak of Ni disappears, while the Mo's one appears with vey low intensity. This data was contradictive with AAS analysis results. It can be shown from the AAS analysis result that Ni and Mo contents in Ni-Mo/natural zeolite catalysts are almost as much as loaded. This indicates that, the form of Ni especially in catalysts is in oxided form, instead of the metal form. The absence of Ni peak in catalyst's diffractogram indicates that loaded Ni in catalysts is in any amorphous forms.

It has been shown that change in natural zeolite crystal structure as a result of impregnation with anions was small. It also undergone in such research [6]

Analysis of FT-IR Spectra

The result of FT-IR analysis of H-zeolite and Ni-Mo/zeolite before and after pyridine adsorption is presented in Fig. 3. It can be shown that the impregnation of Ni-Mo metals on zeolite resulted in narrowing of the peak at 3425 cm^{-1} indicating that a Brønsted acid site is reduced significantly. This decrease in Brønsted acid sites due to the exchange of protons with impregnated metal cations, in this case is Ni. Other evidence showing the decline in the number of Brønsted acid sites are weaker absorption peaks at 2276.00-2499.75 cm^{-1} which is region of pyridine adsorption by zeolite. Absorptions at wave numbers between 300 cm^{-1}-2100 cm^{-1} is significantly reduced which may indicate the changes in the orientation of -OH bond as a result of the introduction of metal Ni and

Table 2. Identification of chromatogram of compounds in *n*-hexane trapper

Retention time (min)	Identified compound by GC-MS	Retention time (min)	Identified compound by GC-MS
3.07	unidentified	4.64	n-hexsane
3.14	iso-butane	4.76	unidentified
3.21	unidentified	4.91	unidentified
3.28	unidentified	5.03	Methyl-cyclopentane
3.44	iso-pentane	5.66	unidentified
3.57	unidentified	5.82	pyridine
4.13	unidentified	8.17	unidentified
4.30	methyl-pentane		

Table 3. Peak width of GC chromatogram as gas trapping result at 350 °C without catalyst, zeolite-catalyzed, and Ni-Mo/zeolite-catalyzed with flow rate of hydrogen of 10 mL/min.

Detected components by GC-MS	Retention time (min)	Area (%)		
		uncatalyzed	H-zeolite	Ni-Mo/zeolite
unidentified	3.07		0.004	0.038
iso butane	3.14		0.018	0.346
unidentified	3.21			0.255
unidentified	3.28			0.044
iso pentane	3.44		0.007	0.314
unidentified	3.57			0.049
unidentified	4.13		0.008	0.081
unidentified	4.76			0.014
unidentified	4.91			0.019
unidentified	5.66		0.006	0.046
pyridine	5.82	0.258	0.098	0.924
unidentified	8.17			0.042

Mo in the zeolite crystal system. The decreasing of -OH absorption peak which means the decrease in acidity of the catalyst is very contradictory to acidity test. Thus we can conclude that the decrease in -OH absorption peak occurs due to the conversion of Brønsted acid sites into Lewis acid sites.

Activity Test of Ni-Mo/Natural Zeolite Catalyst

Pyridine HDN reaction is a reaction involving two reactants, namely pyridine and hydrogen. Reaction order is determined by two components. In order to make the analysis becomes much easier, one of components is fixed, in this case is the feed of pyridine, so that the expected reaction is a reaction of first order (pseudo first order) using hydrogen flow rate as the carrier gas.

Analysis of Reaction Products

Analysis of results was conducted qualitatively to prove the existence of HDN products and quantitatively for the determination of reaction kinetics.

Qualitatively analysis

GC data plot with GC-MS chromatogram successfully identify the six components of the 15 peaks that appear. Nine unidentified peaks due to weak intensity, that's can be shown at Table 2. GC chromatogram data for traps gases produced three successive peaks in the order of greatest intensity is at a retention time of 4.64, 5.03, and 4.30 min. From these data we can conclude that the largest component of the trap is n-hexane, while methylcyclopentane and 2-methyl-pentane is a component of impurities. Thus the appearance of three peaks at the retention time is assumed as a component of the trap n-hexane, so it does not need to be taken into account.

Pyridine HDN product gas fraction which catalyzed Ni-Mo/zeolite more diverse than the HDN product with zeolite catalyst, that's can be shown at Table 3. This fact indicates that the metallic Ni-Mo impregnation led to conversion of some of Brønsted acid sites into Lewis acid sites. Pyridine intermediates activated acid on Lewis acid sites different than those activated by Brønsted acids, both in terms of bond length (distance) pyridine-surface, the polarity of the ring clusters, the charge of each atom in the pyridine ring. Due to these differences lead to different mechanisms with different results. So on with the pyridine HDN catalysts will Ni-Mo/zeolite a more diverse product obtained from the pyridine HDN product with zeolite catalyst without the metal.

In the activity test by varying the hydrogen flow rate, generally the components with low boiling point is detected at any flow rate, only at a flow rate of 40 mL/min numbers of components detected are slight

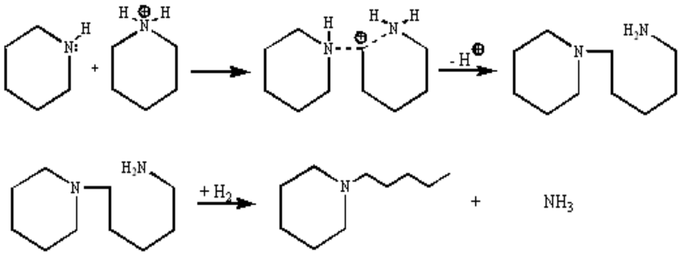

Figure 4. Disproportionation mechanism of piperidine in pyridine HDN

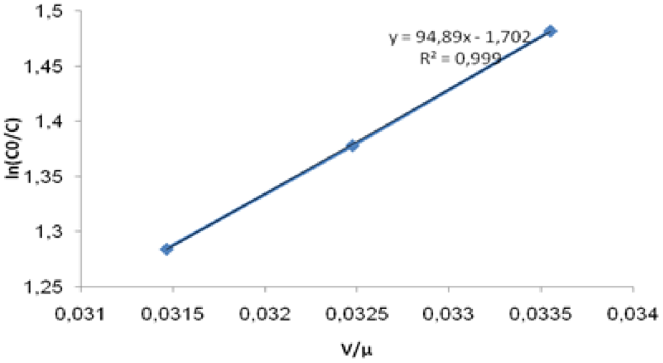

Figure 5. Approximation of rate constant value of pyridine HDN at 350 °C

compared to the others. This is due to its large flow rate causes the contact time between the reactants with the catalyst surface to be relatively short thereby reducing the formation of byproducts. Byproducts can be produced if there is a reaction between the products, the intermediates and products, and between intermediates.

If the reaction took place involving only hydrogen and pyridine HDN, the products produced should be a hydrocarbon with five atoms C i.e. pentane, isopentane or benzene. The presence of isobutane which is a hydrocarbon with four C atoms clearly shows there has been continued due to the formation of cleavage reactions of reactive intermediates.

Quantitative analysis

Impregnation of Ni-Mo in the zeolite increased significantly the products of pyridine HDN. This is due to the both metals Ni and Mo increase the amount of Lewis acid sites on zeolite significantly. By increasing the number of Lewis acid sites on the surface then sticking pyridine on catalyst increases. d-Bands of transition metal encourage a more stable chemisorption, so the intermediates activated-pyridine by Lewis acids in formation of products are more stable. High stability of intermediate products would increase the quantity of HDN because of the probability for reaction with other substrates increases. Whereas for the zeolite catalyst, the formation of more intermediates is due to proton attack of the Brønsted acid sites that are relatively weak bonds, so resulting intermediates form a distance relative to the surface so that the probability of occurring HDN reaction is relatively low.

Evaluation of Rate Constant

Pyridine was believed to be the simplest model molecule to study hydrodenitrogenation (HDN). Although the network of reactions taking place in the HDN of pyridine is now well understood, the study of the kinetics of the HDN of pyridine proved to be extremely difficult. The reason for this difficulty is the occurrence of a side reaction of piperidine, the first intermediate in the HDN of pyridine. Two piperidine molecules disproportionate to N-penthylpiperidine and ammonia as shown in Fig. 4 [16]**.**

Study aimed at developing a kinetic model for the hydrodenitrogenation (HDN) of pyridine [9] dealed with the selectivity of piperidine, one of the products obtained from the HDN of pyridine and with the conversion of pyridine to piperidine. Kinetic parameters were estimated from the results of the experimental data obtained from literature sources where the reactions were carried out in a trickle-bed reactor in the liquid phase over several catalysts at some temperatures. POLYMATH 5.0 software was used to solve the proposed first-order model.

Study on reaction kinetics shows the differences in the intrinsic properties of the active site of different catalysts. Basically, studies on the kinetics of the reaction can define two parameters, reaction rate constant which include the number of sites, and adsorption equilibrium constants that do not depend on the number of sites but on the quality of the active site [15]. In the case of single ring heterocyclic compounds such as pyridine, the kinetics of the reaction proceeds through several stages which have their own pace and have different degrees of contribution to the overall rate.

It has been shown that the HDN products are not a single compound but multicomponents. These facts indicate that the mechanism of the reaction on the catalyst surface is not singular too. In order to determine the HDN reaction rate constant, in this study it was assumed that only sticking pyridine on the catalyst surface which determines the reaction order, while dissociative hydrogen adsorption on the catalyst surface is constant considerably.

It is undeniable that the sticking pyridine may occur at the metal's or zeolite's sites, and also can occur on Lewis and Brønsted acid sites. Differences of sticking at different sites leads to the formation of different intermediates and lead to different products. Products that have not desorbed is possible to engage the side reaction with the intermediates, as shown as

HDN products with branched structures. Therefore HDN reaction rate constant value in this study is a joined constant. By plotting ln (Co/C) against to contact time (V/μ), the graph is obtained as in Fig. 5. Assuming that the pyridine HDN reaction on the catalyst nature Ni-Mo/zeolite a pseudo first order reaction, the value of k was obtained of 94.89 min^{-1} with a 99.9% of correlation index.

CONCLUSION

Impregnation method can generate Ni-Mo/natural zeolite catalyst with good character. Catalyst acidity and crystallinity increased with the success level of impregnation of Ni and Mo respectively of 96.71% and 90.08%. Ni-Mo/natural zeolite catalyst capable of increasing the conversion of pyridine HDN reaction until reaching 71.78% at a temperature of 350 °C and hydrogen flow rate of 10 mL/min with a more diverse product. Assuming that the pyridine HDN reaction followed a pseudo-order reaction kinetics, rate constant k was obtained of 94.89 min^{-1} with a correlation index of 99.9%.

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