DEHYDROGENATION OF HYDRAZINE HYDRATE USING NiCo BIMETALLIC CATALYST SUPPORTED ON NATURAL ZEOLITE (ZA), Z-NaY, Z-HY, Al₂O₃ AND TiO₂

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ABSTRACT

Hydrogen can be produced by dehydrogenation reaction of hydrazine hydrate with help of catalyst material. This study aims to investigate the effect of different catalyst support which is loaded with NiCo bimetallic catalyst toward the dehydrogenation reaction of hydrazine hydrate. Catalyst characterization was carried out using XRD, SAA, and XRF. The catalyst obtained was tested for its catalytic activity through the dehydrogenation reaction of hydrazine hydrate. Surface area analysis was performed for natural zeolite, zeolite NaY, zeolite HY with the value of 40.99 m²/g, 88.94 m²/g, 162.12 m²/g, respectively. NiCo metal alloys impregnated on ZA, Z-NaY, Z-HY, Al₂O₃, and TiO₂ supports produce diffraction patterns at angles of 44.5°, 51.7° and 76.3° with low intensity. The surface area decreases after the NiCo was impregnated on the catalyst support. NiCo(1:3)/TiO₂ catalyst produced the maximum conversion and the best catalyst activity which is 29.71 % for ± 5 minutes with a TOF of 357.79 h⁻¹ and activation energy of 47.33 kJ/mol.

Keywords: Hydrazine Dehydrogenation, Bimetallic, TiO₂, Zeolite Y, Hydrogen Generation.

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INTRODUCTION

Hydrogen is a clean and efficient renewable energy source, due to its combustion only produces water vapor and energy. In addition, the gravimetric energy density of hydrogen reaches 33.3 kWh / kg and the resulting calorific value is three times greater than gasoline.¹ A large number of materials for the formation of hydrogen such as metal hydrides, and molecular hydrides have been studied before, but the development of methods using materials in the form of molecular hydrides is still not widely known. However, materials in the form of molecular hydrides have the potential to have a high hydrogen content. One of the molecular hydrides that can be used is hydrazine hydrate.² Hydrazine hydrate (N₂H₄.H₂O) has a higher hydrogen content (8.0 %) compared to Mg₂NiH₄ metal hydride (3.60 %).³ The metal used as a catalyst in the hydrazine hydrate dehydrogenation reaction can come from the transition group and the noble metal and many researchers recently developed a bimetallic catalyst.⁴⁻⁶

Yang, et al., mentioned that MIL-101 (Metal-organic Framework Based)-supported Ni monometal catalyst showed low activity of hydrogen generation from N₂H₄ at 323 K, and released 4.29 equiv (H₂ + N₂) hydrogen per N₂H₄ for 170 minutes.² In addition, the NiFe / MIL-101 bimetallic catalyst showed higher catalyst activity and selectivity compared to monometals released 4.89 equiv (H₂ + N₂) hydrogen per N₂H₄ for 124 minutes. Men, et al., studied NiFe catalyst with a variation of 1: 3 (Ni: Fe) supported by reduced graphene oxide (r-GO) resulted in a higher conversion with the best catalyst activity compared to variations 3: 1 and 1: 1 (Ni: Fe).⁷ Chen, et al., stated that Ni-based catalysts showed superior catalytic activity and high selectivity to dehydrogenation of hydrazine hydrate for hydrogen formation.⁸ Singh, et al., also observed that the amorphous form of CoB_{0.5-0.01} nanocatalyst showed much better catalyst activity at room temperature with a hydrogen selectivity of 41.8%.⁹ The use of metal oxides (Al₂O₃, CeO₂, La₂O₃, and TiO₂) as supports can significantly improve catalyst performance by providing large metal surface area and strong metal-support interactions.¹⁰

Much research was done using natural zeolite as multifunctional material.^{11,12} Aubakirov mentioned that modifying natural zeolite with molybdenum gives high catalytic activity on thermo-catalytic processing of polymer waste.¹³ The acid site of type Y zeolite also serves as an active site for hydrogenation, hydrocracking and other reactions, this makes the combination of metal and Y type zeolite support to produce a catalyst that is multifunctional.¹⁴

This study focused to examine the effect of zeolite acid sites on hydrazine hydrate dehydrogenation reactions. In addition, catalyst synthesis was carried out with several parameters including variations in the ratio of NiCo metal supported by Al₂O₃ and variations of the catalyst supports such as TiO₂, natural zeolite, Z-NaY and Z-HY. The catalytic activity and the conversion of hydrazine hydrate to hydrogen are determined by the dehydrogenation reaction.

EXPERIMENTAL

Material and Methods

The materials used in this study were nickel (II) chloride hexahydrate (NiCl₂·6H₂O), cobalt (II) chloride hexahydrate (CoCl₂·6H₂O, Sigma Aldrich), sodium borohydrate (NaBH₄, Daejung Chemical), sodium hydroxide (NaOH, Samchun Chemicals), hydrazine monohydrate (N₂H₄·H₂O, Sigma Aldrich), aluminum oxide (Al₂O₃, Alfa Aesar), natural zeolite, TiO₂ rutile powder, aquadest and deionized water (DI).

Preparation of Zeolite

NaY Zeolite was prepared using a modified hydrothermal fusion method with a ratio of 1: 2.4 and heated in a furnace at a temperature of 550 °C for 4 hours. After cooling to room temperature 40 mL of water was added and allowed for 12 hours. The mixed solution was put into a Teflon-coated stainless-steel autoclave to carry out the hydrothermal process at 100 °C for 8 hours. The sample was washed with a solution of hydrochloric acid (HCl 1M) and aquadest to remove the absorbed alkaline to a neutral pH. The product was filtered and dried at 150 °C in an oven, to form zeolite NaY.¹⁵ Zeolite NaY obtained was put into a solution of NH₄NO₃ (1 M) with a ratio of 1: 10. Then it was heated at 100 °C for 2 hours and washed with distilled water to a pH of 6-8, followed by drying for 2 hours at 105 °C. The material was calcined at 550 °C for 2 hours.

Synthesis of Bimetal Catalyst by *In-situ* Impregnation.

Ni monometal was loaded into different support materials (ZA, Z-NaY, Z-HY, Al₂O₃ and TiO₂) with the ratio between metal and catalyst support 10:90 w/w was synthesized by in-situ impregnation method. Briefly, 2.43 g of NiCl₂·6H₂O was dissolved into 20 mL of DI-H₂O, adding an amount of 5.4 g of material supports, stirred and heated at 100 °C until dried and then calcined at 400 °C for 2 hours. Monometal catalyst Co/Al₂O₃ was made with the same method and support-metal composition as the above method. An amount of 2.4224 g of CoCl₂·6H₂O was dissolved into 20 ml of DI-H₂O, stirred and heated at 100 °C until dried and then calcined at 400 °C for 2 hours. The NiCo bimetal catalyst was made with different ratio variations which are then impregnated into the supports. The ratio variations used are 1:1, 1:3 and 3:1, where the total catalyst and the ratio of the total metal loading with the supports are the same as monometallic catalysts.

Catalyst Characterization

The instrument was used in this study were Shimadzu 700 X-Ray Diffraction (XRD), Quantachrome NovaWin version.11 Surface Area Analyzer (SAA), and JEOL Element Analyzer JSX-3211 X-Ray Fluorescence (XRF).

Catalytic Activity Test

Briefly, all catalysts that have been synthesized are subjected to a catalyst test with hydrazine hydrate dehydrogenation reaction to form hydrogen. About 0.5 g catalyst was put into a reactor, then 8 mL of DI-water was added to the reactor and the mixture was stirred. A 2 mL solution containing 10 mmol of NaBH₄ and 10 mmol of NaOH was added and allowed to stand until bubbles disappear in the solution. Furthermore, the dehydrogenation reaction was done by adding 1 mL of hydrazine hydrate to the reactor using a syringe.

During the process, the temperature of the reactor was maintained at 343 K. The gas produced during the reaction was passed through an HCl (1 M) solution and the quantity of the gas produced was measured. The hydrogen selectivity (X) was calculated using eqn.-1 and TOF was calculated using eqn.-2.

$$X = (\lambda/3) \times 100 \% [\lambda = n(\text{H}_2 + \text{N}_2) / n(\text{N}_2\text{H}_4.\text{H}_2\text{O})] \quad (1)$$

$$\text{TOF} = n\text{H}_2 / (n_{\text{NiCo}} \times t) \quad (2)$$

Where t is the reaction time the hydrazine hydrate reaches 50 % conversion, the amount of hydrogen determined by the volume of the generated gas is $n\text{H}_2$, and n_{NiCo} is the amount of Ni and Co.

RESULTS AND DISCUSSION

Brauner-Emmett-Teller (BET) method was used to determine surface area. Another method, namely BJH adsorption was used to determine the pore size distribution of natural zeolites and synthetic zeolites, namely Z-NaY and Z-HY, so that the SAA results can be seen in Table -1.

Table-1: Surface Area Characterization

Catalyst	Surface Area (m ² /g) ^a	Total pore volume (cc/g) ^b	Pore Diameter (nm)
ZA	40.99	0.07	3.93
Z-NaY	88.94	0.26	5.49
Z-HY	162.12	0.29	3.55
NiCo(1:3)/ZA	25.38	0.06	3.56
NiCo(1:3)/Z-NaY	65.84	0.28	13.22
NiCo(1:3)/Z-HY	81.40	0.15	4.87
NiCo(1:3)/Al ₂ O ₃	5.74	-	-
NiCo(1:3)/TiO ₂	7.98	-	-

Remarks: a. Multipoint BET
b. Total pore Volume of P/Po 0.9907

Table-1 shows surface area analysis of different samples. It shows that natural zeolites have a smaller surface area compared with zeolites NaY and Z-HY with the value of 40.99, 88.94 and 162.116 m²/g, respectively. This increase in the surface area indicates that the alkaline fusion process has succeeded in removing impurities and extracting Si in the zeolite so that it can increase the pore diameter, which results in a larger surface area.^{12,16} The increase in the surface area of the zeolite also affects the increase in pore volume. Therefore, the total pore volume in zeolites also increases. Al₂O₃, TiO₂, ZA, Z-NaY, Z-HY-supported NiCo (1:3) bimetal catalysts were analyzed using SAA are presented in Table -1. It can be seen that NiCo (1:3)/Al₂O₃ and NiCo (1:3)/TiO₂ has a very low surface area compared to NiCo(1:3)/ZA. Based on the result, all catalyst support after being impregnated with NiCo (1:3) experienced a significant decrease in surface area. This occurs due to the closure of the pores on the supports by transition metals.

The result of XRD analysis is shown in Fig.-1a and Fig.-1b. Figure-1a shows that the zeolite used was a clinoptilolite type, it can be seen from the diffractogram peaks at $2\theta = 9.8916^\circ$; and $22-30^\circ$. The sharp peak interpreted that clinoptilolite zeolite contains SiO₂ and Al₂O₃, which are the main characteristics of zeolites. This is also following the ICDD database (International Center for Diffraction Data) 39-1383, where the diffractogram peaks show clinoptilolite-Na with the chemical formula $\text{KNa}_2\text{Ca}_2(\text{Si}_{29}\text{Al}_7)\text{O}_{72} \cdot 24\text{H}_2\text{O}$. Zeolite Na-faujasite Y can be seen from the diffractogram peaks at $2\theta = 6.22$; 15.60 ; 20.21 ; 23.62 ; 27.01 ; and 31.36° , where the peaks of the diffractogram correspond to JCPDS 38-0240. The highest intensity was at a peak of $2\theta = 6.18^\circ$, where at that peak the characteristic of zeolite Na-Faujasite Y (Z-NaY). According to Treacy and Higgins, the first zeolite NaY peak will appear at $2\theta = 6-10^\circ$.¹⁷ The zeolite NaY was modified to zeolite HY by the ion exchange method did not show the same dominant peaks as Z-NaY, the result was that the resulting intensity was lower and there was a slight shift in peaks and peaks with a low intensity previously found in Z- NaY disappeared. According to Afreen et al. Z-HY showed the diffraction peak characteristic of the FAU structure at $2\theta = 16.5$; 19.4 ; 21 ; 24.5 ; 28 ; 32 ; and 34.8° with each hkl peak as

follows: (331), (333) (440), (533), (642), (751), and (664).¹⁸ The results of this research that the resulting diffractogram 3 in Figure-1a was an amorphous HY zeolite, this suggested due to partially collapsing zeolite NaY framework in the zeolite NaY modification process, and also the release of the zeolite framework in the calcination process which freed volatile NH_3 compounds from zeolite NH_4Y to form more active Z-HY, thus forming more amorphous.

XRD analysis was carried out on $\text{NiCo}(1:3)/\text{Al}_2\text{O}_3$, $\text{NiCo}(1:3)/\text{TiO}_2$, $\text{NiCo}(1:3)/\text{ZA-clinoptilolite}$, $\text{NiCo}(1:3)/\text{Z-NaY}$ and $\text{NiCo}(1:3)/\text{Z-HY}$ as shown in Figure -1b. The results of the crystal structure analysis of the $\text{NiCo}(1:3)/\text{Al}_2\text{O}_3$ catalyst can be seen in Figure -1b. The X-ray diffraction pattern (XRD) from Figure -1b shows the cubic phase of aluminum oxide corundum with the chemical formula Al_2O_3 -corundum. The peaks of the diffractogram appear at $2\theta = 25.68^\circ$; 35.24° ; 37.85° ; 43.49° ; 52.68° ; 57.58° ; 66.64° ; and 68.31° with the respective fields namely (102), (104); (110), (113), (024), (116), (214), and (300) (JCPDS: 43-1484). The appearance of a diffraction pattern with low intensity at an angle of 33.15° with the Miller index (111) indicates the presence of CoO which leads to an amorphous form, because it only has one diffraction pattern which is following JCPDS 42-1300. In addition, two diffraction patterns of low intensity at $2\theta = 37.37^\circ$ and 43.361° are adjacent to the angles of Al_2O_3 -corundum, which have miller index (111) and (200), respectively. This indicated the presence of NiO from the $\text{NiCo}(1:3)/\text{Al}_2\text{O}_3$ compound (JCPDS 04-0835). The NiO and CoO peaks that appear showed that the Ni and Co metals loaded on the support are still in the form of NiO and CoO. This is because it has not been reduced to metal, therefore the catalyst used for the dehydrogenation reaction of hydrazine hydrate was reduced by the in-situ process, where the reduction was carried out simultaneously with the reaction process.

Based on JCPDS 15-0806 (Co) and JCPDS 04-0850 (Ni) the NiCo diffraction pattern appeared at the angles of 44.5° , 51.85° and 76.90° , respectively, the crystalline diffraction plane (111), (200) and (220). On the other hand, as can be seen in Fig.-1b, there are only two diffraction patterns, namely at an angle of 44.5° and 76.90° , which indicates the formation of a low-intensity NiCo alloy. The resulting low intensity makes the NiCo alloy lead to a low crystallinity form.¹⁹

Fig.-1: The Diffractogram of (a) Zeolite and (b) NiCo Bimetallic Catalyst with Different Support

Figure-1b also shows a typical XRD pattern of anatase TiO_2 , according to JCPDS 21-1272. The diffraction pattern in Figure -1b was dominant in anatase TiO_2 , so that the NiCo alloys that are embedded in TiO_2 only appear in one diffraction pattern at an angle of 44.88° with low intensity. The presence of one peak between 44 and 45° indicates the presence of the NiCo alloy in amorphous form so that the Ni and Co content may produce a very low percentage and the resulted of NiCo purity was also low. The diffraction pattern of NiCo metal alloys (1:3) on zeolite supports, both natural zeolite Lampung clinoptilolite (ZA-clinoptilolite) and zeolite Na-Faujasite-Y (Na-ZY) and zeolite H-Faujasite-Y (Z-HY) can be seen in Figure -1b. The diffraction pattern of natural zeolite clinoptilolite (ZA-clinoptilolite) with NiCo (1:3)/ZA-clinoptilolite catalysts experienced a shift in the area of the diffraction peaks and decreased in intensity at an angle of 9.90° ; and $22-30^\circ$. The shift of the diffractogram peak area and decreased intensity in the NiCo(1:3)/ZA-Clinoptilolite catalyst diffraction pattern showed that the NiCo metal alloy was distributed on the pore

surface of the zeolite. As with the NiCo(1: 3)/Z-NaY catalyst and the NiCo(1: 3)/Z-HY catalyst also experienced a shift in the area of the diffractogram peaks and a decrease in intensity at the angles that are characteristic of Z-NaY and Z-HY supports. The diffraction pattern on the NiCo (1:3)/Z-NaY catalyst at $2\theta = 37.06^\circ$ and 53.48° based on JCPDS 44-0922 shows the presence of an aluminum cobalt nickel phase contained in zeolite Z-NaY. On the other hand, the NiCo (1:3)/Z-HY catalyst when compared to the Z-HY diffraction pattern has decreased the intensity of the peak area at an angle of $23-28^\circ$. This showed that the NiCo (1:3)/Z-HY catalyst leads to an amorphous form.

XRF analysis was used to determine the elemental composition of the catalyst quantitatively. The results are presented in Table -2. The results show that the catalyst supported by zeolite NaY has a decrease in Si concentration compared with natural zeolite. This is during the synthesis of Z-NaY, an alkaline fusion process was carried out using NaOH which functions as a silica binder, where this process undergoes desilication.

Table -2: XRF Analysis Result

No	Element	Concentration (%)				
		NiCo(1:3)/Al ₂ O ₃	NiCo(1:3)/TiO ₂	NiCo(1:3)/ZA	NiCo(1:3)/Z-NaY	NiCo(1:3)/Z-HY
1	Ni	7.25	4.16	8.10	7.61	7.66
2	Co	28.40	13.26	30.82	30.77	29.23
3	Al	49.51	-	4.79	10.17	12.84
4	Si	-	-	26.94	17.97	23.04
5	Ti	-	72.88	-	-	-
6	Na	-	-	-	1.31	-

In the desilication process of the zeolite with alkaline media, the Si atoms in the Si-O-Si are extracted first in an alkaline treatment compared to Si-O-Al. This is due to the presence of AlO_4^- which is capable to stabilize the surrounding Si atoms by rejecting OH^- . So that Si-O-Al is less likely to be attacked by OH^- than Si-O-Si.²⁰ The Na content in Z-NaY in Table-2 shows an exchangeable cation process between Na^+ ions in NaOH with a balancing cation that can be exchanged on the zeolite frame, where Na^+ cations can increase polarization in the gas adsorption process. The results in Table-2 also show an increase in Al and Si in Z-HY supported catalysts, with this increase the Si/Al ratio will also increase so that there was a change in the zeolite framework. Based on the resulting data, the Z-HY material composition showed that the exchange of Na^+ with H^+ ions was successful because the percentage of Na content in the Zeolite HY material was not found. The occurrence of Ni and Co metals in the material indicates that the NiCo alloys are successfully impregnated into the supports. The XRF analysis results in Table-2 also show the percent impregnated. The ratio of the XRF results is following the impregnation carried out, where the composition contained the results is still 1: 3.

Catalytic dehydrogenation of hydrous hydrazine was carried out for all the catalyst support system which stated above. The best variation of the ratio of the active catalyst component will be applied with other supports, namely TiO₂, natural zeolites, synthetic zeolites NaY and HY. The conversion comparison between the active components of the NiCo alloy with different ratios can be seen in Figure-2a and 2b. Figure-2a shows that the NiCo(1: 3)/Al₂O₃ ratio variation results in a higher conversion than other ratio variations. NiCo (1: 3)/Al₂O₃ catalysts get the best results because there was more metal Co content, the higher the Co metal concentration, the higher the conversion obtained. The conversion in catalytic activity is highly dependent on catalyst composition.

The catalyst activity graph is presented in Fig.-2b shows that the Co/Al₂O₃ catalyst has a high turnover frequency (TOF) than the Ni/Al₂O₃ catalyst, with the value of 520.89 h^{-1} and 77.30 h^{-1} , respectively. In addition, it also shows that the NiCo (1:3)/Al₂O₃ catalyst also has a high TOF of 503.11 h^{-1} compared to the NiCo catalyst in the comparison of other ratios. While data show that the TOF value of the Co/Al₂O₃ catalyst was higher than the NiCo (1: 3)/Al₂O₃ catalyst, but the bimetallic catalyst was more selective with the value of 12.48 % and 16.5 %, respectively. The strong metal-metal interaction in the bimetallic system can adjust the bond between the reactants and the catalyst surface, thereby stabilizing the transition state and the reaction intermediate, which leads to an increase in catalyst activity.²¹ NiCo catalyst with a variation

of the NiCo ratio (1:3) was used as an active component that will be impregnated on other supports, namely TiO_2 , natural zeolites, and synthetic zeolites NaY and HY. NiCo catalysts with various NiCo ratios (1:3) impregnated on various types of supports will also be tested for dehydrogenation hydrazine hydrate for hydrogen formation and analyzed for catalyst characterization.

Fig.-2: (a) Time Profile Decompositions of Hydrazine Monohydrate and (b) TOF and Selectivity Calculation on Different Catalyst Systems.

The data on the catalytic activity results of NiCo catalyst (1:3) which are supported by TiO_2 , Al_2O_3 , ZAl-clinoptilolite, and zeolite synthesis NaY and HY are seen in Fig.-3a. Variations were studied to determine the effect of zeolite support on hydrazine hydrate dehydrogenation reaction in hydrogen formation and with other support materials such as Al_2O_3 and TiO_2 . Pillai, et al., examined the degree of acidity in Al_2O_3 and TiO_2 , where the results stated that Al_2O_3 had the highest degree of acidity, and TiO_2 has a basicity property.²² Based on the XRF results on the catalyst, according to previous research which states that Al_2O_3 has the highest degree of acidity, then the NiCo bimetal catalyst which has a higher Al_2O_3 content can be stated to have a high degree of acidity. The level of acidity in the catalyst can affect the resulting conversion and catalyst activity. The activity of the catalyst in the form of frequency turnover (TOF) on this catalyst can be seen in Fig.-3b.

Fig.-3: (a) Time Profile Decompositions and (b) The Catalyst Activity (TOF h^{-1}) with Different Support.

The results of the catalyst test with the lowest acidity level had the highest conversion and catalyst activity, namely the NiCo (1:3)/ TiO_2 which obtained a higher conversion at 155 seconds compared to other catalyst support, at 29.71 % selectivity with a TOF value of 357.79 h^{-1} . Based on the analysis, the best catalyst is the NiCo (1:3)/ TiO_2 catalyst, then the temperature variation was carried out in the hydrazine hydrate dehydrogenation reaction to determine the activation energy.

The result of the hydrogen conversion can be seen in Fig.-4a and Fig.-4b. Figure-4 shows that the NiCo(1:3)/TiO₂ catalyst at 353 K has the highest conversion. The selectivity obtained by the NiCo (1: 3)/TiO₂ catalyst at a temperature of 353 K with a time of 155 seconds is 32.83 %. In addition, at 353 K also produced the best catalytic activity with the TOF of 529.03 h⁻¹, which is shown in Fig.-4a. This suggests that the rate of hydrogen formation increases with increasing reaction temperature, which suggests that a high reaction temperature is useful for increasing the rate of hydrogen generation².

Fig.-4: (a) Time Profile Decompositions, (b) TOF and Selectivity Graph at a Different Temperature, (c) Arrhenius Plot

The resulting TOF value against temperature variations from 323 to 353 K on the NiCo (1:3)/TiO₂ catalyst was used to obtain the value of the activation energy. The activation energy can be found by knowing the rate constant k which is calculated at a different temperature. The slope of the linear portion of each plot and the value of the linear regression equation were calculated. The Arrhenius plot can be seen in Figure -4(c). Figure -4(c) was plotted the X value comes from the $1/T$ calculation and the Y value comes from the $\ln TOF$ calculation as $\ln K$, and the resulting linear line equation can produce activation energy. The activation energy (E_a) obtained on the NiCo (1: 3)/TiO₂ catalyst was 47.33 kJ/mol.

CONCLUSION

This study found that Z-NaY produced from hydrothermal processes has a larger surface area than natural zeolites, namely 88.94 m²/g. The resulting Z-NaY was crystalline while the Z-HY produced from ion-exchange modification was amorphous, but the resulting surface area was larger, which is 162.116 m²/g. The active metal alloy at the variation of the NiCo ratio (1:3) produces high conversion and the best catalyst activity which is 16.50 % for ± 5 minutes with a TOF of 503 h⁻¹. The best type of catalyst support is TiO₂ (NiCo (1:3)/TiO₂) which produces high conversion and the best catalyst activity of 25.708 % for ± 5 minutes with a TOF 357.79 h⁻¹. The results of temperature variations on NiCo (1:3)/TiO₂ were done to obtain activation energy with the value of 47.33 kJ mol⁻¹.

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