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Promotive Effect of Hydrogen in *n*-Hexane Isomerization over Ni/PtHY Catalyst

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ABSTRACT

Bifunctional catalyst containing 0.1 wt% Ni and 0.1 wt% Pt supported on HY were prepared by incipient wetness impregnation method. The properties of the catalyst were determined by XRD analysis and pyridine adsorbed FTIR spectroscopy. The catalytic activities were tested on *n*-hexane isomerization by pulse method in a microcatalytic reactor under atmospheric pressure in the presence of hydrogen or nitrogen carrier gas. XRD result showed the decrease of the crystallinity of PtHY after introduction of 0.1 wt% of Ni. While, the ratio of Lewis to Brønsted acid sites increased after the introduction of Ni on PtHY as evidenced by pyridine adsorbed FTIR spectroscopy. In the presence of hydrogen gas, 0.1 wt% Ni increased the yield of isohexane by about 24 % and decreased the activation energy from 124.1 to 111.2 kJ/mol at the temperature range of 403-423 K. In addition, the activation energy decreased to 48.3 kJ/mol for Ni/PtHY at high temperature range of 478-498 K. The presence of hydrogen as a carrier gas gave a promotive effect on the reaction which led to increase the formation of isohexane and suppress the cracking process. While, the presence of nitrogen as a carrier gas promoted dimerization of *n*-hexane which formed the cracking products.

| *n*-hexane isomerization | PtHY | Ni/PtHY | hydrogen | protonic acid sites |

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1. INTRODUCTION

Isomerization of straight chain alkanes into the corresponding branched isomers is an important reaction to boost the octane quality of a gasoline fraction. Bifunctional catalysts consisting of an acidic oxide and a noble metal show high efficiency in the isomerization of alkanes [1]. Platinum deposited on a support associated with an acidic function catalysts are the most commonly used systems in the industry as well as in the fundamental research [2].

A typical isomerization catalyst is platinum supported on chloride alumina, which is very active and can be operated at low temperatures. However, this catalyst causes corrosion and pollution and is too sensitive to feeding line impurities such as water and sulfur compounds [3]. The use of zeolites as an acidic support can eliminate such problems. Platinum supported on Mordenite zeolite (Pt/H-MOR) has been used commercially for the isomerization of linear alkanes to higher octane branched isomers [4]. This zeolite has strong acidity and is very suitable for these small alkanes giving a high yield of isomers; however, it is less selective in the operating of longer chain paraffin. Pt catalysts supported on three-dimensional channels of Beta and USY zeolites were reported to have higher selectivity and activity than one-dimensional Pt/HMOR in the isomerization of *n*-C₇ and *n*-C₈ paraffins [5-7].

Generally, the supported bimetallic catalysts have several advantageous over the monometallic systems to

achieve higher activity, stability and in some cases, higher selectivity [8]. It has been found that the interaction between the additives and active components of catalysts can influence the activity, selectivity and stability of catalysts via changing the structure, acidity of catalysts and dispersion of the active components of catalysts. The different ways of adding additives, and the different types and amount of additives can lead to different catalytic results.

Our research group has reported the role of hydrogen in a dynamic modification of active sites by molecular hydrogen over Ni/PtHY, MoO₃, Pt/MoO₃, MoO₃-ZrO₂, Pt/MoO₃/ZrO₂, Zn/HZSM6, Ir/Pt-HZSM5, WO₃/ZrO₂ and CrO₃-ZrO₂ catalysts [9-20]. The catalyses based on the concept of "Molecular hydrogen-originated protonic acid sites" in which molecular hydrogen dissociative-adsorbed on specific active sites, such as Pt or acidic sites, to form hydrogen atoms, followed by spillover onto the supports and undergo surface diffusion to form protonic acid sites near Lewis acid sites. This formation of protonic acid sites was proposed as a widely applicable concept for an active site on solid acid catalysis. For instance, incorporation of Zn into HZSM5 catalyst acts as a site to activate the molecular hydrogen to protonic acid sites which are vital in *n*-pentane isomerization [20]. Also, the presence of Ir in HZSM5 catalysts gave higher activity in *n*-heptane isomerization compared to the parent catalyst which due to the presence of higher number of protonic acid sites from molecular

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hydrogen [9]. Thus, the presence of metal is crucial in order to generate strong Lewis acid sites which assist in the formation of protonic acid sites.

Previously, we have examined the potential of Ni/PtHY catalysts with different metal loading (0.1, 1 and 3 wt% Ni) on *n*-pentane isomerization in which we found that 0.1 wt% of Ni on PtHY catalyst gave highest yield of isopentane due to high amount of protonic acid sites on the surface of the catalyst as evidenced by IR and ESR studies [13]. Therefore, in this study, small amount of metals (0.1 wt% Ni and 0.1 wt% Pt) loaded HY catalyst was studied in *n*-hexane isomerization. The effect of carrier gas (H₂ and N₂) were studied in order to elucidate the promotive effect of hydrogen on Ni/PtHY. The role of molecular hydrogen on the reaction was clearly observed and discussed in this work.

2. EXPERIMENTAL

2.1 Catalyst preparation

Prior to the modification, HY zeolite (CBV700, Si/Al: 80, Zeolyst International) was calcined in air at 873 K for 3 h. PtHY was prepared by impregnation of HY with an aqueous solution of hexachloroplatinic acid (H₂PtCl₆.H₂O) (Wako Pure Chemical) followed by drying at 333 K overnight and calcination at 823 K for 3 h in air [21]. The content of Pt was adjusted to 0.1 wt % Pt on HY. The Ni loaded PtHY was prepared by impregnation of PtHY with Ni²⁺/DMF solution followed by drying at 333 K overnight and calcination at 823 K for 3 h in air. Prior to this, the Ni²⁺/DMF solution was prepared by electro-generated method according to the procedure as Jalil et al. reported in Ref. [22] and the amount of Ni was adjusted to 0.1 wt% Ni on PtHY. In brief, a N,N-dimethylformamide solution (DMF) (Merck) containing tetraethylammonium perchlorate (TEAP) and naphthalene was added to one compartment of a cell equipped with a nickel plate (2 cm×2 cm) as an anode and a platinum plate (2 cm×2 cm) as a cathode. The electro-generation of Ni²⁺ was then executed at 273 K. The prepared catalysts were denoted as PtHY and Ni/PtHY for Ni free and 0.1 wt % Ni loaded on samples, respectively.

2.2 Catalyst characterization

Powder X-ray diffraction (XRD) pattern was measured using a Bruker Advanced D8 diffractometer with $\lambda = 1.5406 \text{ \AA}$ at 40 kV and 40 mA. The percentage crystallinity of the sample was measured using calibration curve which was plotted from the mixing of SiO₂ and HY. The main peak of XRD pattern of all catalysts (not shown) at 6.39° was used in the calibration curve to determine the crystallinity of catalyst.

FTIR measurements were performed on an Agilent Cary 640 FTIR spectrometer equipped with a high-temperature stainless steel cell with CaF₂ windows. A sample of 30 mg in the form of a self-supported wafer was

evacuated at a rate of 5 K/min to 623 K for 3 h. It was then cooled to room temperature and IR spectra were recorded. To estimate the concentration of Brønsted and Lewis acid sites, the activated samples were exposed to 2 Torr of pyridine at 423 K for 30 min, followed by evacuation at 573 K for 30 min to remove the physisorbed pyridine and spectra were recorded at room temperature.

2.3 Catalytic reaction

Isomerization of *n*-hexane was conducted in a fixed-bed quartz reactor with an interior diameter of 8 mm at atmospheric pressure and in a temperature range of 375-675 K. The thermo-couple was directly inserted into the catalyst bed to measure the actual pretreatment and reaction temperatures. The catalyst was sieved and selected in the 20–40 μm fraction. Prior to the isomerization, the catalyst was activated in oxygen stream for 1 h followed by hydrogen stream for 3 h at 673 K and cooled down to a reaction temperature in a hydrogen stream [23]. A dose of *n*-hexane (0.5 μl) was passed over the activated catalyst and the products were trapped at 77 K before being flash-evaporated into an online 6090N Agilent Gas Chromatograph equipped with VZ-7 packed column and FID detector.

The yield of the reaction was determined by multiplication of conversion of *n*-hexane (*X*) and selectivity to isohexane (*S_i*). The conversion and selectivity were calculated according to Eq.(1) and Eq.(2), respectively.

$$X = \frac{\sum A_i - A_{n\text{-hexane}}}{\sum A_i} \times 100\% \quad (1)$$

$$S = \frac{\sum A_i}{\sum A_i - A_{n\text{-hexane}}} \times 100\% \quad (2)$$

Where *A_i* are corrected chromatographic area for particular compound.

3. RESULTS & DISCUSSION

3.1 Structural and textural features of the catalysts

XRD patterns (not shown) for PtHY and Ni/PtHY were observed and attributed to the FAU structure characterized by the intense reflections at 2θ equal to 6.4, 10.45, 12.25 and 16.1° which was found to be in good agreement with a standard reference [24]. The crystallinity of the sample decreased to 96% and 91% for PtHY and Ni/PtHY compared to the pristine HY zeolite (100%) due to the partial collapse of zeolite framework or pore blockage by metal (Pt and Ni) species (Table 1). In addition, the peaks of Ni and Pt were not observed in the present study. This may be attributed to the size of the particles, which

might be well dispersed on the surface of the catalyst. Hence, the size of the Ni particles may be smaller than 4 nm as reported by Cui et al. [25] for Ni-W based catalyst.

Table 1 presents the amount of Lewis (absorbance band at 1455 cm^{-1}) and Brønsted (absorbance band at 1545 cm^{-1}) acid sites calculated from the IR spectra of adsorbed pyridine. The introduction of Ni decreased both Lewis and Brønsted acid sites by 3.2 and 8.7 %, respectively. The decreasing may be related to the amount of Al in the framework in which the total amount of acid sites was proportional to the Al content of the framework [26]. However, the ratio of Lewis to Brønsted acid sites (L/B) increased after the introduction of Ni by 5.9%. The increase in the ratio may be due the present of Ni metal-exchanged with PtHY which contributed to the partial collapse of the structure of the zeolite and thus lead to increase the population of Lewis acid sites with concomitant decrease of Brønsted acid sites. The population of Brønsted acid sites decreased since they are directly related to tetrahedrally coordinated framework aluminum species.

Table 1 Physicochemical properties of the samples

Catalyst	Crystallinity (%)	L ₁₄₅₅	B ₁₅₄₅	L ₁₄₅₅ /B ₁₅₄₅
PtHY	96	0.086	0.046	1.87
Ni/PtHY	91	0.083	0.042	1.98

3.2 Isomerization of *n*-hexane

Table 2 shows the result for conversion and selectivity at 120 min time on stream. Upon addition of 0.1 wt% Ni on PtHY catalyst, the conversion increased to 69 % and the selectivity significantly increased up to 75 %. Higher yield of isohexane by Ni/PtHY catalyst was mainly due to the higher ratio of Lewis to Brønsted acid sites of the catalyst. The role of Lewis acid sites was observed by Volkova et al. in sulfated zirconia system, in which the different density of Lewis acid sites were obtained by varying the pH from 7 to 11.5 during catalysts preparation. As a result, higher density of Lewis acid sites led to higher activity in *n*-hexane isomerization [27].

The effect of the temperature in the isomerization of *n*-hexane was studied and the result is shown in Fig. 1. It can be concluded that the increase of the reaction temperature always increased the conversion of *n*-hexane markedly. At high temperatures, the selectivity to isomerization decreased gradually due to the formation of more cracking products. In comparison to PtHY, Ni/PtHY exhibited a rather higher conversion and selectivity towards isomerization at wide range of reaction temperature (423-673 K). In addition, the degree of decreasing of selectivity over Ni/PtHY was much lower than that of PtHY. Furthermore, it also showed that the optimal reaction temperature for Ni/PtHY was 573 K, in which, the high

selectivity to isomerized products (75%) coupled with a rather high conversion of *n*-hexane (69%) were obtained.

Table 2 Catalytic performances (at time on stream = 120 min) and activation energy (E_a) of *n*-hexane isomerization over all catalysts (Temperature = 573 K, H₂ flow = 10 ml/min).

Catalyst	PtHY	Ni/PtHY
Conversion (%)	50	69
Selectivity (%)		
C ₁ -C ₅	37	18
<i>i</i> -C ₆	55	75
C ₇₊	8	7
Yield of <i>i</i> -C ₆ (%)	28	52
E_a (403-423 K) (kJ/mol)	124.1	111.2
E_a (478-498 K) (kJ/mol)	60.3	48.3

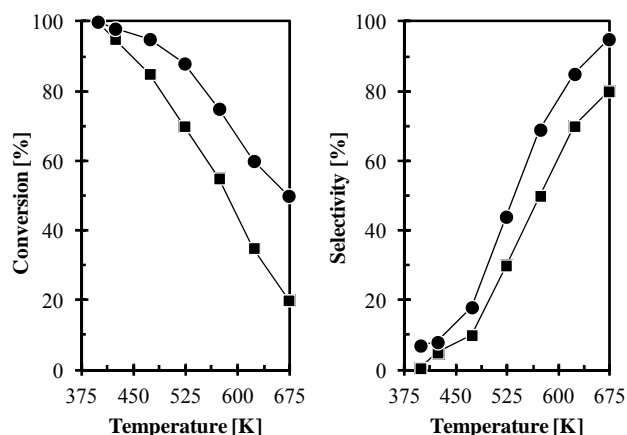


Fig. 1 Influence of temperature on conversion and selectivity of PtHY (■) and Ni/PtHY (●) in *n*-hexane isomerization.

The apparent activation energy (E_a) can be calculated from the slope of an Arrhenius plot as shown in Fig. 2. After the introduction of Ni, the E_a values markedly decreased due to the enhancement of the catalytic activity (Table 2). Two different activation energy regions were observed for both PtHY and Ni/PtHY. At temperature range of 403-423 K, the E_a values were 124.1 and 111.2 kJ/mol for PtHY and Ni/PtHY, respectively. While for higher temperature of 478-498 K, the E_a values are 60.3 and 48.3 kJ/mol for PtHY and Ni/PtHY, respectively. The introduction of Ni decreases about 10.4 and 20 % of E_a for low and high temperature regions. The discrepancy of the

activation energy at different temperatures region suggested that some different reaction mechanism or different rate determining step present on both PtHY and Ni/PtHY [28]. Based on the results by Matsuda et al. [29], the activation energies for PtHY for *n*-pentane and *n*-heptane isomerization in the range of 523-573 K were 143 and 99 kJ/mol, respectively. Therefore, the values of activation energy on *n*-hexane isomerization over PtHY and Ni/PtHY in this experiment are comparable to the values of the previous report.

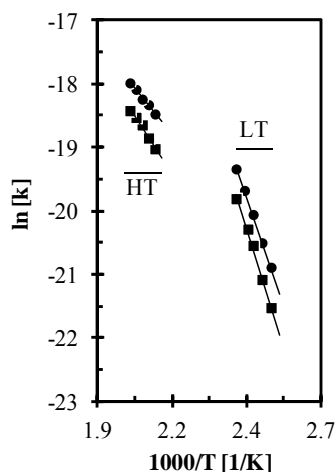


Fig. 2 Arrhenius plot for low (LT) and high (HT) reaction temperature for PtHY (■) and Ni/PtHY (●).

The effect of carrier gas (H_2 and N_2) was tested on Ni/PtHY catalyst at 423 K and the results are shown in Fig. 3. The outlet was composed of isohexane, cracking products (C_1 , C_2 , C_3 , C_4 and C_5) and residual *n*-hexane as well as higher hydrocarbon (C_{7+}). In this experiment, the carrier gas was sequentially switched from hydrogen to nitrogen and switched back to hydrogen in order to examine the promotive effect of hydrogen on Ni/PtHY catalyst. The presence of molecular hydrogen on specific active species, such as nickel species, may contribute to inhibition of coke formation and providing active sites on the catalyst surface. Although not shown here, *n*-hexane isomerization was not appreciable with the powder form of the NiO particle (selectivity: 0%, conversion < 1%) regardless of the carrier gases used. The absence of location to stabilize active sites is caused by the inability of the catalyst to generate protonic acid sites from molecular hydrogen as the catalytically active sites. In the first five doses under hydrogen stream, the catalyst exhibited high selectivity for *n*-hexane isomerization. The *n*-hexane conversion is slightly maintained when the carrier gas of hydrogen was switched to nitrogen but the selectivity to isohexane decreased continuously by 89% of its original value. In the presence of nitrogen, the thermal cracking occurred selectively to produce by-products. Contrarily, according to the previous report, in the isomerization of *n*-pentane over Zn/HZSM5 catalyst, the rate of conversion decreased to almost zero in

the presence of nitrogen which was due to the absence of protonic acid sites generated by molecular hydrogen [14]. The activity and stability of Ni/PtHY recovered slowly with the pulse number when the carrier gas was switched back to the hydrogen. The selectivity to isohexane was almost recovered to the initial condition and this clearly showed the promoting effect of hydrogen on the Ni/PtHY catalyst.

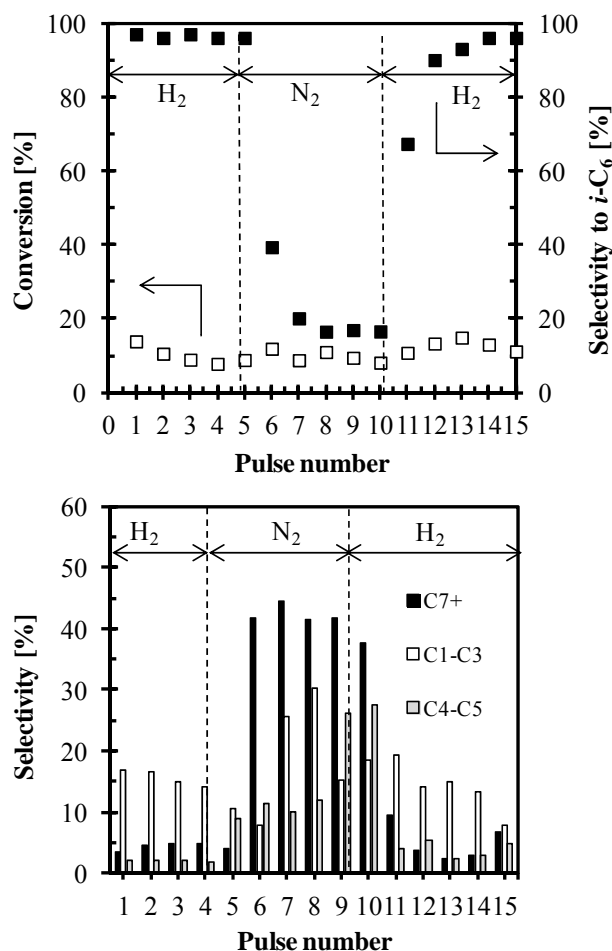


Fig. 3 Effect of carrier gas H_2 and N_2 on the conversion and selectivity to the products in *n*-hexane isomerization over Ni/PtHY sample.

The formation of C_{1-3} is dominant in the first hydrogen stream with selectivity 10% at the fifth dose. When the carrier gas of hydrogen switched to nitrogen, the selectivity to C_{1-3} and C_{4-5} increased continuously with the pulse number. The formation of C_{7+} (heptane and others long alkane) suddenly increased after switching to nitrogen stream to approximately 40% of selectivity. However, there is a presence of small amount of isohexane in the products that may be due to the remaining of hydrogen gas in the stream or the formation of protonic acid sites from *n*-hexane over the Ni and/or Pt sites. In addition, the presence of C_{7+} suggested that the mechanism of *n*-hexane isomerization via cracking followed by dimerization reaction. In the report by

Viswanadham et al. [30] which studied the isomerization of *n*-hexane over Pt-HBEA catalysts, they were also suggested that the formation of branched alkane in the absence of hydrogen (in the presence of nitrogen) is due to the route of cracking and dimerization (alkylation) reaction. In our report, the decrease of selectivity to isohexane after switching the carrier gas to nitrogen was due to the gradual exhaustion of adsorbed hydrogen (protonic acid sites) on the surface of the catalyst. The absence of molecular hydrogen may prevent the formation of protonic acid sites, resulting in the inhibition of isomerization. At this state, the Lewis acid sites may be restored to their original strength. At the last five doses, the selectivity of C₁–C₃ decreased to about 6% when the carrier gas was switched back to hydrogen gas and the trend was similar to the first five dose in the hydrogen stream.

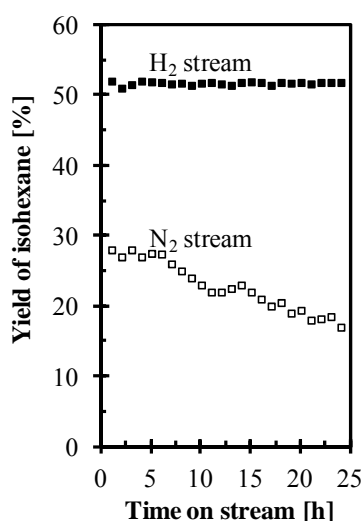


Fig. 4 Effect of stability under H₂ and N₂ carrier gas for Ni/PtHY sample in *n*-hexane isomerization

The promotive effects of hydrogen were observed in the formation of isohexane and in the suppression of cracking products over Ni/PtHY catalyst. Removal of the hydrogen stream may cause a decrease in the activity and stability of the Ni/PtHY catalyst. While, the role of nitrogen plays an important role in dimerization reaction and can be seen in the second five dose and above. Yang et al. [31] reported the promotive effects of hydrogen on *m*-xylene transformation over NiS/Al₂O₃-USY hybrid catalysts. The high activity of the reaction is attributed to the presence of molecular hydrogen which dissociated on the NiS site and the spillover hydrogen then migrated to USY surface. The promotive effects of hydrogen on *n*-pentane isomerization over Pt/SiO₂ mixed with H-Beta were reported by Kusakari et al. [32]. They discussed that the participation of H⁺ and H⁻ was initiated by dissociative adsorption of hydrogen on a metal followed by spillover of a hydrogen atom to support the acidic center. The positive reaction order with respect to hydrogen was explained by enhancement of acid strength

by spilt-over hydrogen. Besides Pt, Pd metals also effective to activate the molecular hydrogen. For instance, Pd can effectively improve the activation of H₂ over Fe–Cu–Co based catalyst and as a result, higher space-time yield and selectivity of alcohols were obtained [33].

Fig. 4 demonstrates the sustainability of the Ni/PtHY catalyst studied for a period of 24 h at 573 K in the presence of hydrogen and nitrogen as carrier gas. The catalytic system in hydrogen stream showed a slightly maintain in activity within 24 h. While, the reaction tested in nitrogen stream showed a deactivation which started at 7th dose and slowly decreasing by 39 % at the last dose. Deactivation of Ni/PtHY in N₂ stream may be caused by the presence of coke deposits during the reaction and lead to the three following modes: (i) limitation of the access of *n*-hexane to the active sites, (ii) blockage of the access to the sites of the cavities (or channel intersections) in which the coke molecules are located and (iii) blockage of the access to the sites of the pores in which there are no coke molecules [34].

4. CONCLUSION

Small amount of Ni (0.1 wt%) loaded on PtHY decreased the crystallinity of PtHY and increased the ratio of Lewis to Bronsted of the catalyst. The introduction of Ni on Pt/HY increased the activity and stability in *n*-hexane isomerization with activation energy of 124.1 and 111.2 kJ/mol for PtHY and Ni/PtHY, respectively. Hydrogen gas played an important role in the formation of isohexane while nitrogen promoted to the dimerization reaction. The role of hydrogen in this study follows to the concept of “Molecular hydrogen-originated protonic acid site” in which the hydrogen promoted to the formation of protonic acid sites which is vital in the isomerization.

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