

Negative effect of Ni on PtHY in *n*-pentane isomerization evidenced by IR and ESR studies

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Abstract

Ni/PtHY with different Ni loadings was prepared by impregnating HY with hexachloroplatinic acid solution and Ni²⁺/N,N-dimethylformamide solution. An increase in the Ni loading decreased the crystallinity, specific surface area and meso-micropores of the catalysts. Ni interacted with hydroxyl groups to produce IR absorption bands at 3740–3500 cm⁻¹. Increasing Ni loadings resulted in a decrease in the intensities of the broad bands at 3730–3500 cm⁻¹ and the sharp band at 3740 cm⁻¹ with simultaneous development of new absorbance band at 3700 cm⁻¹ that was attributed to (–OH)Ni. The acidity of the samples did not significantly change with Ni loadings up to 1.0 wt%, which indicated that Ni mostly interacts with non-acidic silanol groups (terminal- and structural-defect OH groups). The presence of Ni decreased the activity of PtHY toward the isomerization of *n*-pentane because of a decrease in the number of active protonic-acid sites that formed from molecular hydrogen. IR and ESR studies confirmed that Pt facilitated the formation of protonic-acid sites from molecular hydrogen, whereas Ni, even when combined with Pt, didn't exhibit such ability. The absence of protonic-acid sites from molecular hydrogen significantly decreased the yield of *iso*-pentane and markedly increased the cracking products.

Key words

Ni; Ni/PtHY; *n*-pentane isomerization; hydrogen; protonic acid sites

1. Introduction

The interactions between molecular hydrogen and supported metal catalysts have been widely explored in recent years [1]. The nature of spillover hydrogen, in particular, has been investigated with respect to the characteristic properties of the catalyst [2,3]. The protonic-acid sites that originate from the spillover hydrogen are responsible for the formation of active sites for several acid-catalyzed reactions such as alkane isomerization [4,5] and hydrogenation of benzene [6,7]. The proton is formed via the dissociative adsorption of hydrogen atoms onto the support, followed by surface diffusion of the spillover hydrogen to a Lewis-acid site and donation of an electron from hydrogen atom to the Lewis-acid

site [8]. The proton thus formed is located on the surface oxygen atom near the Lewis-acid site and acts as a catalytically active protonic-acid site.

The generation of the protonic-acid sites has been observed in the IR spectra of adsorbed pyridine for several catalysts, including WO₃-ZrO₂ [9–11], Pt/WO₃-ZrO₂ [10,12], Pt/SO₄²⁻-ZrO₂ [5,13], Zn/H-ZSM5 [14] and even metal-free HZSM5 [14]. However, the rates of the spillover vary with the type of catalyst and the state of the surface where hydrogen atoms undergo surface diffusion [15]. For instance, hydrogen adsorption on Pt/WO₃-ZrO₂ is faster than that on WO₃-ZrO₂, because of the existence of Pt sites on WO₃-ZrO₂ that could facilitate the spillover of hydrogen atoms [10,12]. A similar phenomenon was observed in the Pt/MoO₃ system, in which the Pt sites are required for the hydrogen adsorption [16].

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In this report, we have studied the effects of Ni and Pt on HY catalysts for the isomerization of *n*-pentane in the presence of hydrogen. In general, nickel-based catalysts exhibit high stability and activity [17,18], and they are promising isomerization catalysts because of their lower cost; furthermore, they exhibit a strong ability to adsorb hydrogen in comparison with other metals, such as Pd, Pt and Ru [19]. However, we have found that the presence of nickel decreases the activity of the PtHY catalyst toward the isomerization of *n*-pentane in the presence of hydrogen. In fact, the addition of less than 1.0 wt% Ni on PtHY slightly changed the physical properties of HY and only slight acidity of the HY catalyst was changed. Based on IR and ESR studies, we concluded that Pt enhanced the formation of active protonic-acid sites from molecular hydrogen, whereas Ni, even when combined with Pt, didn't exhibit such ability. Therefore, the presence of Ni decreased the formation of protonic-acid sites from molecular hydrogen, which led to a decrease in the activity of PtHY toward the isomerization of *n*-pentane.

2. Experimental

2.1. Catalyst preparation

Commercial HY (Zeolyst) with a Si/Al atomic ratio of 80 was used as a support catalyst. Prior to modification, HY was calcined at 823 K for 3 h in air. PtHY was prepared by impregnating HY with an aqueous solution of hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$) (Wako Pure Chemical); the impregnated catalyst was subsequently dried at 383 K overnight and calcined at 823 K for 3 h in air. The content of Pt was adjusted to 0.1 wt%.

The Ni-loaded PtHY (Ni/PtHY) was prepared by impregnating PtHY with Ni^{2+} /N,N-dimethylformamide solution, followed by drying at 383 K overnight and calcination at 823 K for 3 h in air. The Ni^{2+} /N,N-dimethylformamide solution was prepared according to the previously reported method [20]. The content of Ni was adjusted to 0.1, 1.0 and 3.0 wt% on PtHY. The samples were denoted as PtHY, 0.1Ni/PtHY, 1.0Ni/PtHY and 3.0Ni/PtHY for Ni-free, 0.1 wt% Ni, 1.0 wt% Ni and 3.0 wt% Ni, respectively, loaded onto PtHY catalysts. To allow the observation of the effects of Ni on the HY support, 0.1 wt% Ni was impregnated on HY, followed by drying at 383 K overnight and calcination at 823 K for 3 h in air. For the analysis of Ni, the powder form of Ni was obtained by centrifugation of Ni^{2+} /N,N-dimethylformamide solution at 20,000 rpm for 30 min, followed by filtration, drying at 383 K overnight and calcination at 823 K for 3 h in air [13].

2.2. Catalyst characterization

Powder X-ray diffraction patterns were obtained on a Bruker Advanced D8 using $\text{Cu } K_\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA. Nitrogen physisorption measurements were performed on a Quantachrome Autosorb-1. Prior to the adsorption measurements, the samples were outgassed at

573 K for 3 h. The adsorption was performed at 77 K.

2.3. Infrared spectroscopy

IR spectroscopy was used to evaluate the concentration of hydroxyl groups and the acidity of samples. The sample was activated at 623 K for 3 h under flowing hydrogen [21], followed by evacuation at 623 K for 1 h. To investigate the acidity of the catalysts, the activated samples were exposed to 2 Torr pyridine at 423 K for 30 min, followed by evacuation at 573 K for 30 min to remove the physisorbed pyridine. The generation of protonic-acid sites from hydrogen molecules on the catalyst was observed as follows [9,10]. The pyridine-preadsorbed catalyst was exposed to 50 Torr hydrogen at room temperature. The catalyst was then stepwise heated from room temperature to 573 K in increments of 50 K. All spectra were recorded at room temperature on a Perkin-Elmer Spectrum GX FTIR spectrometer.

2.4. Electron spin resonance

A JEOL JES-FA100 ESR spectrometer was used to observe the formation of electron holes or unpaired electrons in vacuo heating, and to observe the interaction of the electron holes or unpaired electrons with electrons formed from molecular hydrogen through a hydrogen-spillover mechanism at room temperature to 473 K. The catalyst was outgassed at 673 K for 3 h, followed by the introduction of 50 Torr gaseous hydrogen at room temperature. The catalyst then was heated to room temperature (298 K), 323, 373, 423 and 473 K in the presence of hydrogen. All spectra were recorded at room temperature.

2.5. Isomerization of *n*-pentane

The isomerization of *n*-pentane was performed in a microcatalytic pulse reactor at 573 K. Prior to the isomerization, the catalyst was activated in an oxygen stream at 773 K for 1 h. The catalyst was subsequently heated in a hydrogen stream at 773 K for 3 h and then cooled to 573 K in a hydrogen stream. A dose of *n*-pentane (43 μmol) was passed over 0.4 g activated catalyst and the products were trapped at 77 K before being flash-evaporated into an online 6090N Agilent gas chromatograph equipped with a VZ-7 packed column and an FID detector.

The yield of the reaction was determined by the conversion of *n*-pentane and the selectivity to *iso*-pentane. The conversion and selectivity were calculated according to Equations (2) and (3), respectively.

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

$$S_{iso} = \frac{\sum A_i}{\sum A_i - A_{n\text{-pentane}}} \times 100\% \quad (2)$$

where, A_i is the corrected chromatographic area for a particular compound.

3. Results and discussion

XRD patterns of HY and the modified HY samples (Figure 1) exhibited the most intense diffraction peaks at $2\theta = 2^\circ - 50^\circ$, which are attributed to the Faujasite-type structure of zeolite Y (JCPDS card 77-1549). The peaks of Pt and Ni were not detected in the pattern of the modified HY sample, because the amounts of Pt and Ni might be below the detection limit of the diffractometer. Pt and Ni can also be considered evenly distributed on the surface of the support. The introduction of Pt on HY did not significantly change the crystallinity of the HY zeolite, whereas the presence of Ni collapsed the HY zeolites long-range crystal symmetry. The crystallinity of HY decreased to approximately 78% and 56% for 1.0 wt% and 3.0 wt% Ni contents, respectively.

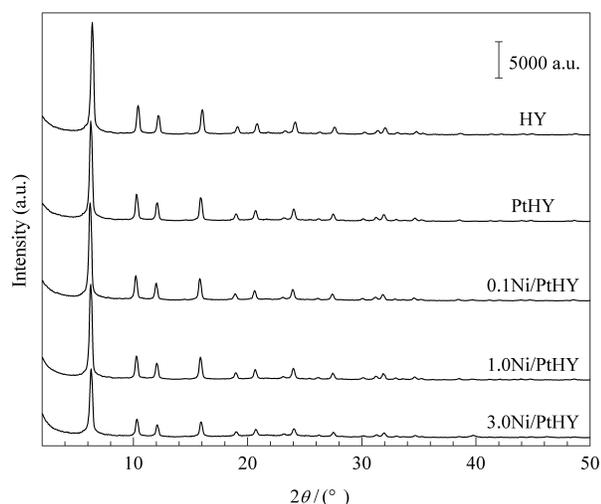


Figure 1. XRD patterns of different catalysts

Figure 2 shows the pore distribution of the HY and modified HY samples. The presence of Pt and Ni decreased both the numbers of meso- and micro-sized pores, which led to a decrease in the specific surface areas and the total pore volumes of the samples (Table 1). The presence of Pt and 0.1 wt% Ni did not substantially change the distribution of the mesopores. The appreciable changes were observed for Ni contents greater than or equal to 1.0 wt%. A significant change in the micropores was observed for 3.0 wt% Ni-loaded PtHY, in which the number of pores less than 12 Å in diameter decreased markedly. Furthermore, XRD results showed that the addition of 3.0 wt% Ni collapsed the crystallinity of HY therefore significantly decreasing the total volume and specific surface area of HY. The change in the pore-size distribution might be caused by the change of crystallinity, and/or Pt and Ni blocked the entrance of the porous network or occupied the inner pores of the HY zeolite. Moreover, Cañizares et al. [22] reported that Ni species was attached to the external surface of H-mordenite, because the particle size of Ni species was larger than the pore size of the support. Although we cannot determine the location of Ni with certainty, the presences of Pt and Ni changed the physical

properties of HY: the specific surface area, total pore volume and crystallinity of the samples follow the sequence of $\text{PtHY} > 0.1\text{Ni/PtHY} > 1.0\text{Ni/PtHY} > 3.0\text{Ni/PtHY}$. With the exception of the 3.0Ni/PtHY catalyst, the properties of the catalysts were not substantially different.

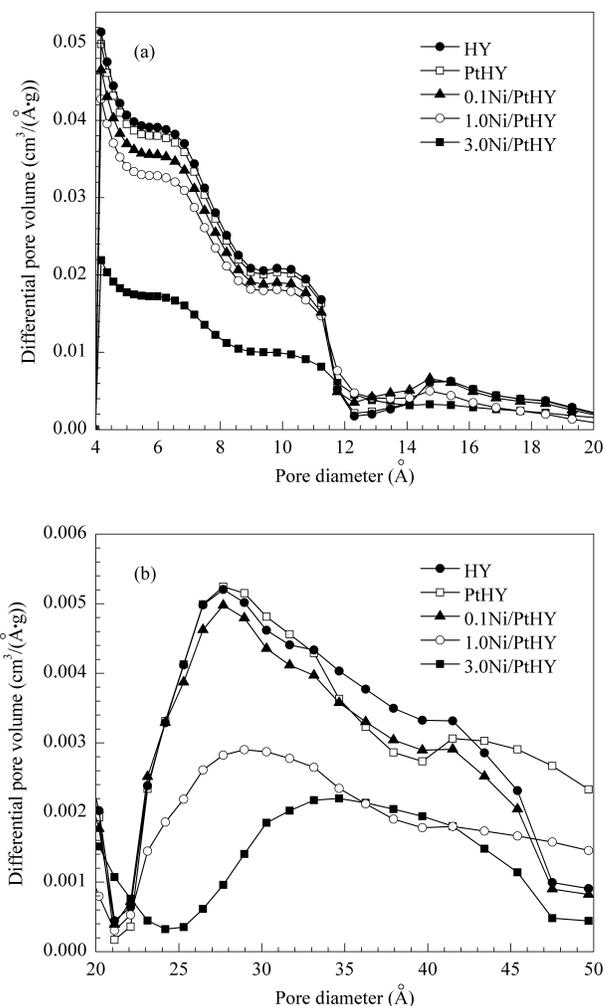


Figure 2. Pore-size distribution curves for the micropore (a) and mesopore regions (b) obtained for different catalysts

Table 1. Physical properties of parent and modified HY catalysts

Catalysts	Ni content (wt%)	BET surface area (m^2/g)	Total pore volume (cm^3/g)
HY	0	752	0.5544
PtHY	0	743	0.5409
0.1Ni/PtHY	0.1	701	0.5195
1.0Ni/PtHY	1.0	637	0.4066
3.0Ni/PtHY	3.0	363	0.3494

The amount of Pt was 0.1 wt%

Figure 3 shows the IR spectra of the hydroxyl groups and acidic-site regions for the HY and modified HY samples. The HY sample exhibited a strong absorbance band at 3740 cm^{-1} , which is ascribed to the terminal silanol groups (Si-OH). Broad absorbance bands in $3500 - 3720\text{ cm}^{-1}$ range are ascribed to OH stretching vibrations and are related to

the structural environment and the lattice framework. The broad bands at 3700, 3680, 3660 and 3635 cm^{-1} correspond to the absorbance bands of perturbed silanol groups, bridged hydroxyl groups, protons in six-ring windows of the cages and OH groups in the ten-member channels [23]. The introduction of Pt did not significantly change the absorbance bands in the region of the hydroxyl groups (Figure 3a(2)), whereas further introduction of Ni changed the absorbance bands of the hydroxyl groups considerably (Figure 3a(3) to 3a(5)). The addition of 0.1 wt% Ni eliminated the broad bands in the range of 3500–3720 cm^{-1} and partially decreased the band assigned to the terminal silanol groups at 3740 cm^{-1} . As the Ni loading was increased to 3.0 wt%, the intensity of the sharp absorbance band at 3740 cm^{-1} decreased markedly, and a new peak appeared at 3700 cm^{-1} . The new peak at 3700 cm^{-1} may be related to the interaction of Ni with OH groups ($-(\text{OH})\text{Ni}$) located on the surface of the zeolite framework. These results indicate that Ni may interact with both acidic and non-acidic hydroxyl groups on the surface of the zeolite framework, even though the number of acidic hydroxyl

groups was extremely low compared with that of non-acidic hydroxyl groups on this HY.

FTIR spectroscopy was performed on pyridine-adsorbed samples to identify the types and strength of the acid sites by enabling the adsorption bonds formed between the acidic sites and the probe molecules to be easily identified. Figure 3(b) shows the pyridine-adsorbed FTIR results, which indicate that the presence of Pt and Ni in the HY did not significantly change the bands at 1545 and 1450 cm^{-1} that correspond to the Brønsted- and Lewis-acid sites (Figure 3b). However, the acidity of the sample decreased markedly after the addition of 3.0 wt% Ni. This change may be caused by the excess amount of Ni on the surface, which hindered the basic probe molecules access to the acidic sites. Alternatively, the change may be caused by the collapse of the crystallinity of the sample, which would lead to a decreased number of bridged OH groups and unsaturated metal cations on the framework. The addition of Ni on the HY zeolite either did not significantly change the acidity of the catalyst (Figure 3b dotted line). Based on these results, we suggest that Pt and Ni did not directly influence the acidity of the samples, even if Ni interacted with the hydroxyl groups on the surface of the HY zeolite; rather, Pt and Ni physically affected the samples by covering the surface, blocking the pores and destabilizing the framework structure of HY. These effects, in turn, led to the collapse of the frameworks crystallinity. However, the presence of Pt and Ni on the surface of HY significantly affected the activity of the catalyst toward the isomerization of *n*-pentane. The presence of Pt markedly increased the activity of HY toward the conversion of *n*-pentane, and the yield of *iso*-pentane was increased approximately 9- and 6-fold, respectively, because of the role of Pt in the enhancement of the isomerization in the presence of hydrogen [24], as shown in Table 2. In contrast, the addition of Ni decreased the activity of HY toward the isomerization of *n*-pentane. The presence of Ni on HY suppressed the isomer product and accelerated the cracking reaction to produce C_1 – C_4 products. The addition of 0.1 wt% Ni on PtHY slightly decreased the yield of *iso*-pentane and significantly increased the selectivity to *iso*-pentane. Further addition of Ni on PtHY significantly decreased the activity of the catalyst. The yield of *iso*-pentane was decreased to 8.9% for 3.0 wt% Ni content, and the selectivity to *iso*-pentane was less than 10%. We are not certain what causes the differences between Pt and Ni in *n*-pentane isomerization over HY, in which Pt and Ni enhanced the isomerization and cracking reaction, respectively. However, we could mention here that the high selectivity to cracked product of 3Ni/PtHY sample may be accounted for this result in terms of its poor metal-acid balance and low amount of protonic acid sites by which lowered the amount of isomer product and thus increase the cracked products. The cracked products also may be due to the presence of coke which covers the active sites of the catalysts. Based on these results, we suggest that the activity of the HY catalyst toward the isomerization of *n*-pentane is strongly affected by the presence of metal species on the HY surface. In general, the presence of Pt increased the activity of the catalysts, but the

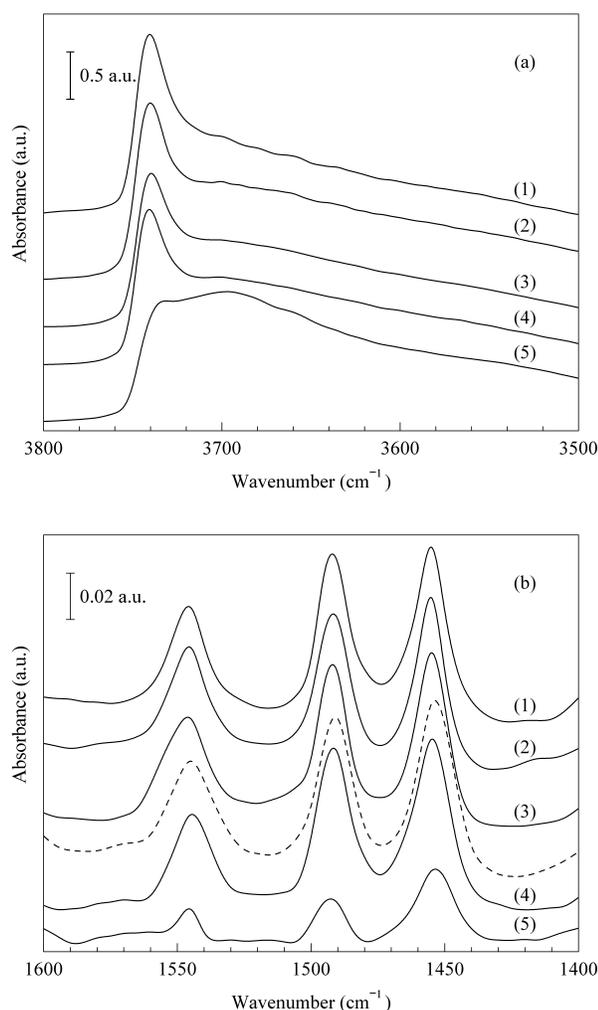


Figure 3. IR spectra in the hydroxyl stretching region (a) after activation in vacuum at 673 K and adsorbed pyridine (b) for (1) HY, (2) PtHY, (3) 0.1Ni/PtHY, (4) 1.0Ni/PtHY and (5) 3.0Ni/PtHY catalysts. The dotted line represents the 0.1Ni/HY catalyst

presence of Ni lowered the yield and increased the amounts of cracking products.

Table 2. Product distribution of *n*-pentane isomerization at 573 K in the presence of H₂

Catalysts	Conversion (%)	Selectivity (%)			Yield of <i>i</i> -C ₅ (%)
		C ₁ -C ₄	<i>i</i> -C ₅	C ₆₊	
HY	6.9	0.5	93.0	6.5	6.4
0.1Ni/HY	9.8	59.2	37.7	3.1	3.7
PtHY	53.9	33.9	64.1	2.0	34.6
0.1Ni/PtHY	40.9	9.0	88.9	2.1	36.4
1.0Ni/PtHY	37.7	23.2	73.6	3.2	27.1
3.0Ni/PtHY	93.9	90.1	9.5	0.4	8.9

Several research groups have reported the effects of Pt and Ni toward the isomerization of alkanes. The catalysts that contained Pt showed a positive reaction rate with respect to hydrogen [24]. Most authors have noted that hydrogen activated on platinum is a source of protons and hydride species. Watanabe et al. [25] have demonstrated that Pt-SO₄ZrO₂ catalyst is more active, more selective and more stable for the isomerization of light naphtha than SO₄ZrO₂. Kartikayen et al. [26] have observed the role of Ni on the isomerization of *n*-heptane. They noted that the incorporation of Ni on Pd/HY at concentrations of 0.1 to 0.5 wt% Ni decreased the selectivity to *iso*-heptane, because of the improper balance between the acid sites of the support and the bimetallic particles [26]. Similar results have been reported by Eswaramoorthi et al. [27], who have observed that the ratio of isomerized to cracked product in *n*-heptane isomerization also decreased when Ni was loaded in the range of 0.1 to 0.5 wt% on Pt/HY. In another report, Jordão et al. [28] observed that an excessive amount of Ni on a Pt/HY catalyst lowered the activity of HY toward *n*-hexane isomerization, because of the unreduced Ni cations and a low metal dispersion.

The effect of Ni on other support catalysts, such as HZSM5, has also been reported. Yin et al. [29] have observed that the Ni/HZSM5 catalysts with different Ni loadings (6,

10 and 11 wt%) decreased olefin formation with increasing Ni loadings. It must be noted that the formation of olefins is a prerequisite to the formation of *iso*-paraffins. Olefins are formed by dehydrogenation of *n*-paraffins fed over the metallic hydrogenation-dehydrogenation function and they are adsorbed on the acidic surface of the catalyst as carbonium ions by proton addition. After skeletal isomerization, they desorb as *iso*-olefins and are subsequently hydrogenated to the corresponding *iso*-paraffins. Hence, the author concluded that the hydrogenation activity of Ni is low because of Ni's low ability to hydrogenate olefin.

To elucidate the role of Ni in *n*-pentane isomerization over PtHY in this experiment, we observed the interaction of molecular hydrogen on the surface of the catalyst using in situ FTIR and ESR spectroscopies. Figure 4 shows the IR spectra of hydrogen adsorption over pyridine-pretreated 0.1Ni/PtHY and 3.0Ni/PtHY at 298–573 K. The protonic-acid sites increased and the number of Lewis-acid sites simultaneously decreased with the increase of heating temperatures. Although the catalysts exhibit differences in the intensity and formation rate of protonic-acid sites, the mechanism of the conversion of Brønsted- to Lewis-acid sites for both catalysts is essentially the same. The formation of active protonic-acid sites was interpreted based on the concept of "molecular hydrogen-originated protonic acid sites", in which the molecular hydrogen dissociatively adsorbs onto the specific sites. The adsorption is followed by the spillover of atomic hydrogen onto the catalyst surface and the formation of protonic-acid sites that are generated by the release of electrons near the Lewis-acid sites [4,5]. Figure 5 shows the variation in the number of protonic-acid sites formed as a function of temperature for PtHY and Ni-loaded PtHY. For all of the catalysts, an increase in the heating temperature increased the number of protonic-acid sites formed, whereas an increase in the amount of loaded Ni gradually decreased the ability of the catalyst to form protonic-acid sites from molecular hydrogen. This result suggests that the presence of Ni on PtHY inhibited the

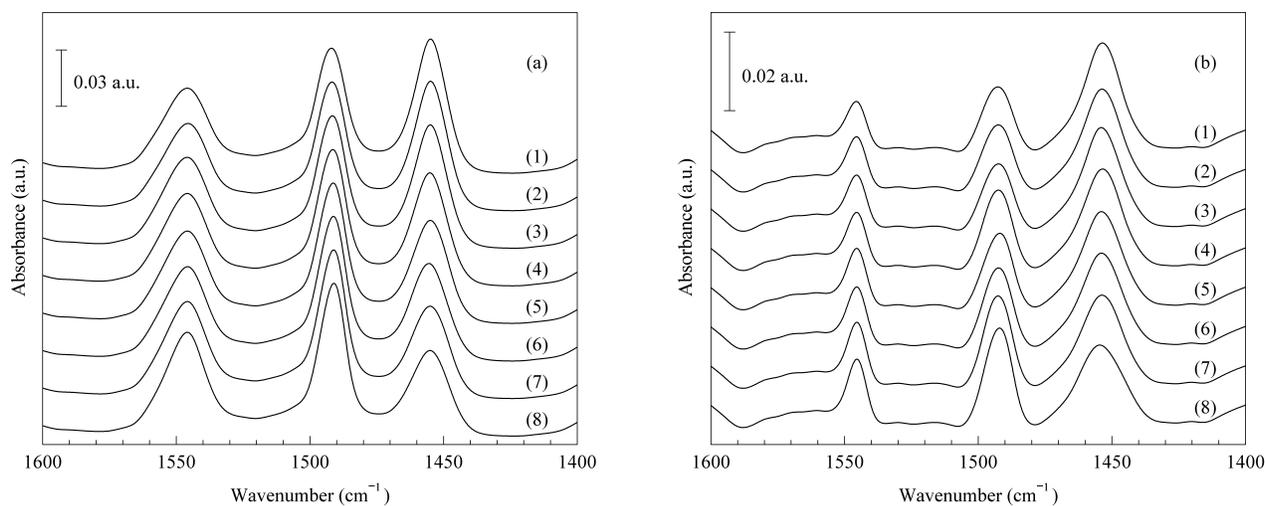


Figure 4. Spectral changes for pyridine adsorbed on (a) 0.1Ni/PtHY and (b) 3.0Ni/PtHY catalysts, heated in hydrogen at (1) Before exposure to hydrogen, (2) 298 K, (3) 323 K, (4) 373 K, (5) 423 K, (6) 473 K, (7) 523 K and (8) 573 K

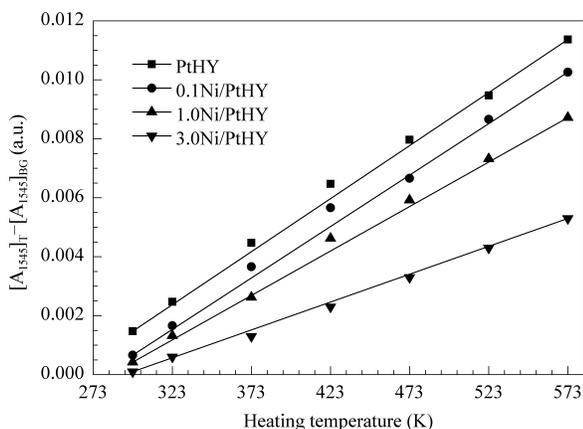


Figure 5. Variation on the change of absorbance at 1540 cm^{-1} with heating in hydrogen for different catalysts. $[A_{1545}]_{BG}$ represents the intensity of the Brønsted-acid sites before hydrogen adsorption

formation of protonic-acid and/or the presence of Ni-occupied sites, which are required for the formation and stabilization of protonic-acid sites. Figure 6 shows the FTIR spectra of hydrogen adsorption on pyridine-preadsorbed Ni/HY, which indicate that no protonic-acid sites were formed in the temperature range of 423 to 573 K. These results substantiate the role of Pt and Ni on HY, of which Pt facilitates the formation of protonic-acid sites from molecular hydrogen, whereas Ni exhibits no ability to facilitate the formation of protonic-acid sites from molecular hydrogen, even at 573 K.

ESR spectroscopy, which detects and identifies electron species with high sensitivity, has been applied to observe the interaction of molecular hydrogen with PtHY and Ni/HY at

temperatures that ranged from room temperature to 473 K [30,31]. When the Pt/HY and Ni/HY catalysts were heated at 673 K for 3 h in vacuo, the intensity of the ESR signal increased at $g = 1.9866$, which corresponds to the trapped electrons or unpaired electrons that have localized on metal cations (electron-deficient metal cations) [32], as shown in Figure 7. The formation of trapped electrons or unpaired electrons may be related to the desorption of hydroxyl groups from the surface of the catalyst, which subsequently leaves electron-deficient metal cations. The introduction of gaseous hydrogen, followed by heating at 323, 373, 423 and 473 K, resulted in the formation of electrons and protonic-acid sites that should decrease the signal at $g = 1.9866$, because the electrons will be trapped in the electron-deficient metal

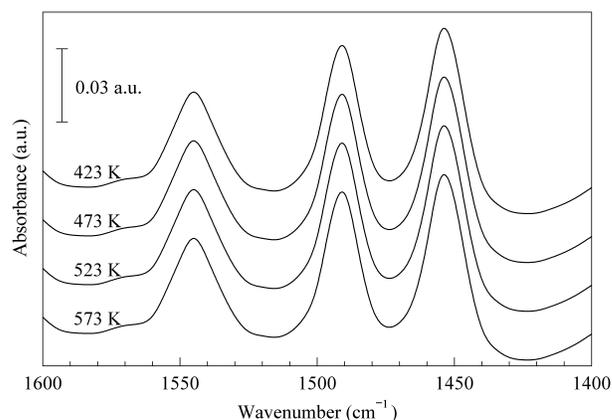


Figure 6. FTIR spectra of hydrogen adsorption on pyridine-preadsorbed 0.1Ni/HY catalyst at different temperatures

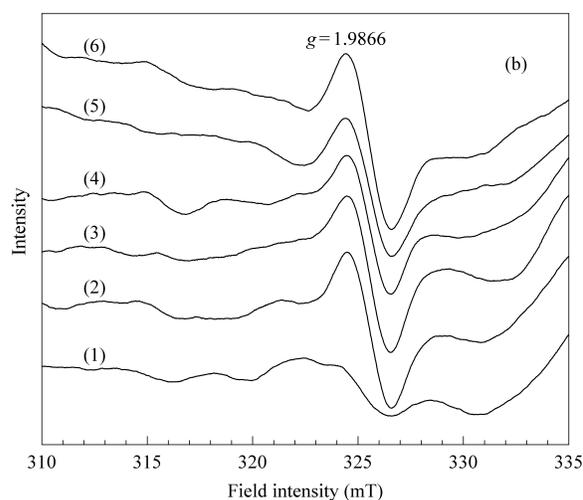
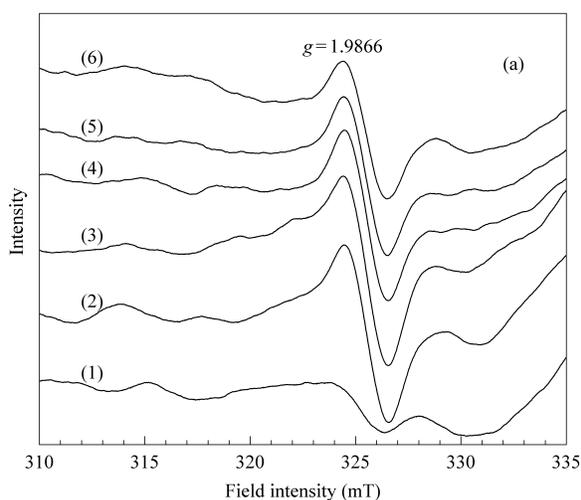


Figure 7. ESR signals of (a) PtHY and (b) NiHY. (1) Before outgassing; (2) After outgassing at 673 K and heated in the presence of molecular hydrogen at (3) 323 K, (4) 373 K, (5) 423 K and (6) 473 K

cations, and protonic-acid sites will be stabilized near the surface oxygen atoms. In the case of Pt/HY catalyst, the heating in the presence of hydrogen partially eliminated the ESR signal related to the trapped electrons or unpaired electrons at $g = 1.9866$, because of the formation of electrons via

the hydrogen spillover mechanism. In contrast, the heating of Ni/HY catalyst in the presence of hydrogen did not significantly change the ESR signal. The differences between PtHY and Ni/HY in the formation of electrons can be clearly observed in the plot of the variation in the intensity as a func-

tion of heating temperature, as shown in Figure 8. For PtHY catalyst, the signal at $g = 1.9866$ began to decrease in intensity during the initial heating, and decreased 50% at 473 K. In contrast, the ESR signal for Ni/HY remained essentially unchanged, even when the sample was heated to 473 K. Based on this result, we suggest that Pt spilt atomic hydrogen onto the surface, and this effect was followed by the formation of protonic-acid sites and the release of electrons, which were trapped by electron-deficient metal cations. However, metal Ni exhibits no such ability to form electrons from molecular hydrogen. The results of ESR study are consistent with FTIR study of hydrogen adsorption on pyridine-adsorbed catalysts.

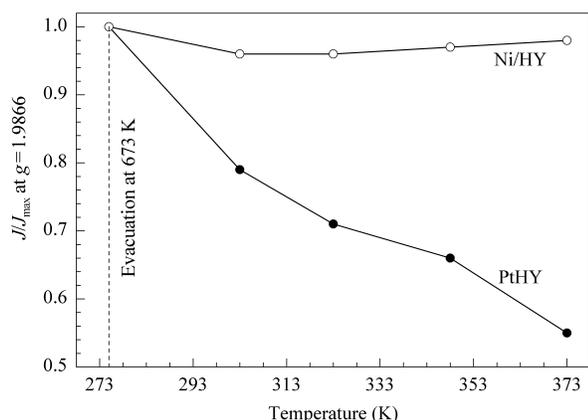


Figure 8. Variation in the intensity of the ESR signal at $g = 1.9866$ as a function of heating temperature. Filled symbols represent the intensity of signals before the samples were heated in the presence of hydrogen

Figure 9 shows the effects of Ni loading on PtHY on the formation of protonic-acid sites and the yield of *iso*-pentane. Although the addition of 0.1 wt% Ni slightly increased both the number of protonic-acid sites and the yield of *iso*-pentane, in general, Ni loading decreased the ability of the catalyst to form protonic-acid sites and successively decreased the yield of *iso*-pentane. The negative effect of Ni on PtHY in the isomerization of *n*-pentane may be related to the inability

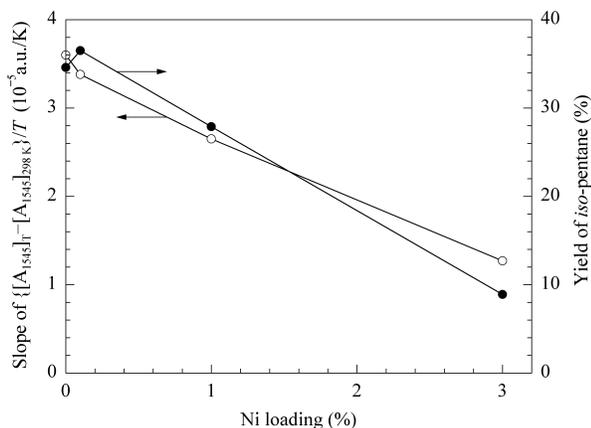


Figure 9. Effect of Ni loading on the rate of formation of protonic-acid sites (●) and the yield of *iso*-pentane (○). $[A_{1545}]_{BG}$ represents the intensity of Brønsted-acid sites before hydrogen adsorption

of Ni to spillover hydrogen, and hence its inability to form protonic-acid sites and electrons.

4. Conclusions

The addition of 1.0 wt% or less Ni slightly changes the physical properties of PtHY, but does not significantly change the acidity of the catalyst. Ni interacts with acidic and non-acidic hydroxyl groups to produce new IR band at 3700 cm^{-1} that corresponds to Ni bonded with hydroxyl groups ($-\text{OH}$)Ni. The presence of Ni decreases the activity of PtHY toward the isomerization of *n*-pentane, because the ability of the catalyst to form active protonic-acid sites from molecular hydrogen is decreased. ESR and FTIR studies reveal that Pt facilitates the formation of protonic-acid sites from molecular hydrogen, whereas Ni, even in combination with Pt, exhibits no such ability. The absence of protonic acid sites from molecular hydrogen significantly decreases the yield of *iso*-pentane and markedly increases cracking products.

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