Sulfur Tolerance of Zeolite Beta-Supported Pd-Pt Catalysts for the Isomerization of *n*-Hexane

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Bifunctional bimetallic M-Pt/H-Beta (M = Cu, Ga, Ni, and Pd) catalysts were prepared and applied to the isomerization of *n*-hexane. The sulfur-containing feed was prepared by addition of thiophene in pure *n*-hexane to have 500 ppmw sulfur. Sulfur in the feed brought about a substantial decrease in the catalyst performance and the sulfur deactivation of bifunctional Pt/H-Beta turned out to be a two step irreversible process caused by metal poisoning followed by coking. To test their effect on the sulfur tolerance, various second metals (Cu, Ga, Ni, and Pd) were added to monometallic Pt/H-Beta catalysts. Unfortunately, all of these, except for Pd, greatly decreased the sulfur tolerance of the original Pt/H-Beta catalyst. Regardless of the preparation method or the Pd/Pt atomic ratio of the bimetallic Pd-Pt series, all the bimetallic catalysts showed high sulfur tolerance, in comparison to the monometallic Pt/H-Beta and Pd/H-Beta. The metal dispersion and the hydrogenation activity decreased in the Pd-Pt series compared to Pt/H-Beta. However, the amounts of sulfur adsorbed and coke deposited on the sulfur-deactivated Pd-Pt/H-Beta were much lower than those on Pt/H-Beta, Pd/H-Beta, and the other M-Pt/H-Beta catalysts. It seems obvious that the Pd-Pt bimetallic interaction in Pd-Pt/H-Beta increased the amount of electron deficient metal sites. Therefore, it may be concluded that Pd-Pt bimetallic interaction inhibits irreversible sulfur adsorption and thereby reduces sulfur-induced coke formation. This is why the Pd-Pt series maintained high activity under sulfur deactivation conditions.   © 1998 Academic Press

Key Words: sulfur tolerance; Pd-Pt bimetallic; H-Beta; isomerization; *n*-hexane.

INTRODUCTION

Supported platinum catalysts are well known for their high activities for hydrogenation, paraffin hydroisomerization/hydrocracking and naphtha reforming. These catalysts, however, are susceptible to poisoning by sulfur (1). Therefore, the deep hydrodesulfurization of feedstocks to lower the sulfur levels down to levels which particular catalysts can tolerate and the development of high thiotolerant catalysts, are of interest in a scientific and practical point of view. The susceptibility to poisoning by sulfur arises from the fact that there is a strong binding of sulfur to metal. Even

a small amount of sulfur in the feeds can saturate the metal surface and thereby deactivate the catalyst after prolonged operation. It has been reported that the sulfur tolerance of platinum-loaded catalysts could be influenced by various factors such as preparation methods, pretreatment conditions (2, 3), support acidity (4–6), and bi- or multimetallic interactions (7–12). Platinum supported on acidic supports is generally accepted to be more sulfur tolerant than those on nonacidic supports. The high sulfur tolerance of platinum supported on acidic supports, compared to that on nonacidic supports, is most often ascribed to the electron-deficient nature of platinum resulting from the interaction with acidic (electron acceptor) support (4–6, 13).

Pt/zeolite catalysts for the hydroisomerization/hydrocracking on *n*-paraffins are thus more sulfur tolerant than Pt/KL aromatization catalysts but still suffer from poisoning by sulfur. According to a pilot plant test by Zarchy *et al*. (14), even amounts as small as 5 ppmw of sulfur in the feed cause substantial decrease in the performance of Pt/zeolite isomerization catalysts. Because about half of the refineries worldwide do not hydrodesulfurize the C_5/C_6 fraction of the gasoline pool and there is a strong drive to produce isoalkanes by hydroisomerization/hydrocracking of heavier petroleum fraction (15, 16), it is very important to gain a better insight into the mechanism of bifunctional Pt/zeolite catalyst deactivation by sulfur and to improve its sulfur tolerance. However, less attention has been directed to the effect of sulfur on the catalytic properties of bifunctional Pt/zeolite for hydroisomerization/hydrocracking reactions. In recent years, Jao *et al*. studied the stability of Pt/H-mordenite against sulfur-bearing feed (2) and the effect of Ni addition (10) on the performance of Ni-Pt/H-mordenite for light naphtha isomerization. The compromise between metal dispersion and metal cluster stability was suggested to be responsible for the performance maintenance but Ni-Pt bimetallic interaction promoted fuel gas formation and caused rapid deactivation by sulfur compared to Pt/H-mordenite. The bimetallic bifunctional Pt-Ge/H-mordenite and Pt-Sn/H-mordenite catalysts were introduced in a patent by Dufresne *et al*. (17) for the isomerization of *n*-paraffin.

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In this study, we investigated the effect of sulfur on the performance of Pt/H-Beta. To improve the sulfur tolerance of Pt/H-Beta, various bimetallic M-Pt/H-Beta catalysts were prepared and tested for the isomerization of n-hexane. The results indicate that sulfur deactivation of bifunctional Pt/H-Beta is an irreversible process caused by platinum sulfide formation followed by coke deposition. It was also found that Pd-Pt bimetallic interaction gives rise to enhanced sulfur tolerance while maintaining activity similar to monometallic Pt/ and Pd/H-Beta catalysts for the isomerization of pure n-hexane. Bimetallic Pd-Pt/H-Beta catalysts were characterized by H_2-TPD, hydrogen chemisorption, FT-IR spectroscopy of CO adsorbed catalysts, and benzene hydrogenation.

EXPERIMENTAL

Catalysts preparation. Zeolite H-Beta was obtained from PQ Corp. (CP811BL-25, Si/Al = 12.5, BET surface area of 750 m^2/g). Before metal loading, H-Beta was calcined in air at 540°C for 5 h. Noble metals were introduced into H-Beta by both incipient wetness impregnation (IWI) and ion-exchange (IE). In ion-exchange, the liquid/solid ratio in slurries was 100 ml per gram of zeolite. The slurry was stirred at room temperature for 48 h. Then the slurry was filtered and thoroughly washed in distilled water to remove chloride ions. Metal precursors used in this study are given in Table 1. In bimetallic M-Pt/H-Beta catalysts, the contents of Pt and the second metal M were 1.0 and 0.5 wt%, respectively. The prepared monometallic Pt/H-Beta and Pd/H-Beta and bimetallic M-Pt/H-Beta were dried at 110°C overnight and then heated at a rate of 0.5°C/min in O_2 flow (1 l/min g-cat) up to 350°C. The catalyst was maintained at 350°C for 2 h and allowed to cool to room temperature in He flow. Reduction was then performed in H_2 flow (200 cc/min g-cat) by raising the temperature at a rate of 2°C/min to 500°C and the temperature was held at 500°C for 1 h.

TABLE 1

Preparation of Pt, Pd, and M-Pt/H-Beta Catalysts

Catalyst	Method	Pt (wt%)	M (wt%)	Metal precursor	H/M[a]
Pt	IWI[b]	0.5	0.0	Pt(NH$_3$)$_4$Cl$_2$	
Pt	IWI	1.0	0.0	Pt(NH$_3$)$_4$Cl$_2$	0.40
Pd	IWI	0.0	1.0	Pd(NO$_3$)$_2$ · 2H$_2$O	0.11
Pd-Pt(a)	IWI	1.0	0.5	Pd(NO$_3$)$_2$ · 2H$_2$O	0.25
Pd-Pt(b)	IE[c]	1.0	0.5	Pd(NO$_3$)$_2$ · 2H$_2$O	
Pd-Pt(c)	IWI	0.5	0.5	Pd(NO$_3$)$_2$ · 2H$_2$O	0.19
Ni-Pt	IWI	1.0	0.5	Ni(NO$_3$)$_2$ · 6H$_2$O	0.13
Ga-Pt	IWI	1.0	0.5	Ga(NO$_3$)$_3$	0.17
Cu-Pt	IWI	1.0	0.5	Cu(NO$_3$)$_2$ · 3H$_2$O	0.31

[a] Obtained from H_2 chemisorption (M = Pt and/or Pd).
[b] IWI (incipient wetness impregnation).
[c] IE (ion-exchange).

Catalytic activity test. All the catalysts were pretreated *in-situ* in the same way as mentioned in the *catalysts preparation* and cooled to the reaction temperature in H_2 flow. The hydroisomerization of n-hexane was conducted in a fixed-bed down-flow reactor with H_2/n-hexane molar ratio of 6.0 at atmospheric pressure. The reaction temperature was in the range of 240–300°C. Typically, 0.1 g of catalyst was loaded onto a porous frit inside a 1-cm ID Pyrex tube. Pure n-hexane (purity >99.5%, Fluka) was fed to the reactor in H_2 flow by a microfeeder at a WHSV of 1.58 h^{-1}.

Sulfur deactivation test. Sulfur-containing feed was prepared by adding specific amounts of thiophene (purity >99+%, Janssen) to pure n-hexane to have 500 ppmw sulfur. To investigate sulfur tolerance of the catalysts, the reaction test was carried out at 280°C with WHSV of 1.58 or 6.59 h^{-1} and H_2/feed molar ratio of 6.0. The reaction products were analyzed by FID in a GC containing an HP-PONA (crosslinked methylsilicon, 50 m × 0.2 mm × 0.5 μm) capillary column.

Benzene hydrogenation. To measure the hydrogenation activities of various bimetallic M-Pt/H-Beta catalysts, hydrogenation of benzene was conducted at 100°C with H_2/benzene molar ratio of 9.8 and WHSV of 29.3 h^{-1} at atmospheric pressure. For this reaction, 30 mg of catalyst was used with the same pretreatment and product analysis conditions described above.

H_2-TPD. For temperature programmed desorption of hydrogen, the catalyst was pretreated as described above. After reduction, the catalyst bed was cooled to room temperature in a flow of H_2. The bed was flushed with N_2 and the TPD was started by increasing the temperature at a rate of 15°C/min. The amount of H_2 desorption was detected with TCD and an interfaced computer was used for data recording.

Hydrogen chemisorption. Hydrogen chemisorption was performed in a static vacuum volumetric apparatus at room temperature to investigate metal dispersion. Two isotherms were obtained to determine the total amount of adsorbed H_2 and the amount of weakly adsorbed H_2. The volume of strongly adsorbed H_2 was determined by subtracting the two isotherms and extrapolating the results to zero pressure. The procedures are described elsewhere (18). The values of H/M (M = Pt and/or Pd) are given for various catalysts in Table 1.

FT-IR spectroscopy of CO adsorbed catalysts. Self-supporting 40-mg catalyst wafers (diameter 13 mm) were pretreated *in-situ* under the same operation conditions as mentioned above in a glass cell fitted with NaCl windows and high-vacuum stopcocks. Afterwards, the cell was evacuated to a pressure of approximately 10^{-3} Torr and cooled to room temperature in vacuum. Then, samples were exposed

to CO at 20 Torr for 15 min. The spectra were recorded after evacuation to the base pressure under increasing mode of evacuation temperature from room temperature to 200°C. Background spectrum was recorded in advance for each of the samples at the same temperature as the sample and subtracted from the sample spectrum to remove the perturbation of the spectrum due to the absorption of the zeolite frameworks. The spectra were recorded on a Nicolet Impact 410 Fourier-transform spectrometer with a resolution of 4 cm^{-1} and scan number of 100.

Elemental analysis. The amount of coke deposited and sulfur adsorbed on the sulfur deactivated catalysts were analyzed by CHNS analyzer (LECO, CHNS-932).

RESULTS

Sulfur Deactivation of the Bifunctional Pt/H-Beta Catalyst

To investigate the effect of sulfur in the feed on the activity of bifunctional Pt/H-Beta, the accelerated sulfur deactivation test was conducted with pure *n*-hexane and sulfur-containing feed at 280°C with WHSV of 6.59 h^{-1}. The activity of Pt/H-Beta is plotted against the reaction time in Fig. 1. With pure *n*-hexane, the activity remained constant for 6 h of the run. When the feed was switched to the sulfur-containing feed, the activity rapidly dropped off to about 20% of that with sulfur-free feed in 15 min. After about 5 h of the run with sulfur-containing feed, the activity was considerably lowered. Even after switching to the sulfur-free feed, the activity did not recover.
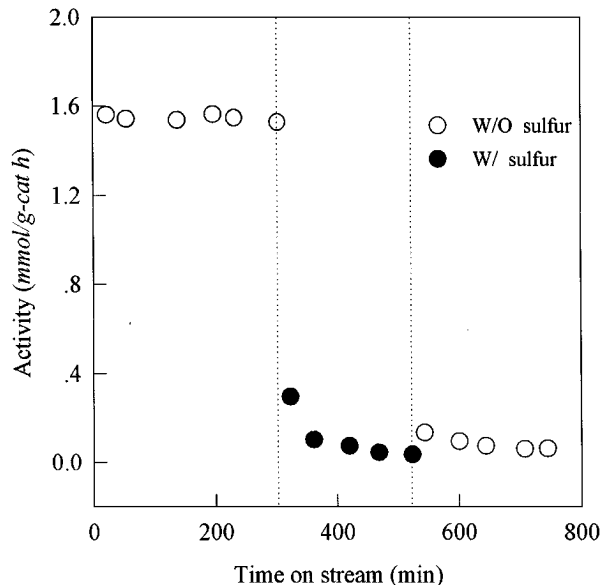

FIG. 1. Irreversible sulfur deactivation of Pt/H-Beta at 280°C (500 ppmw S, WHSV = 6.59 h^{-1}, H$_2$/*n*-hexane = 6.0).

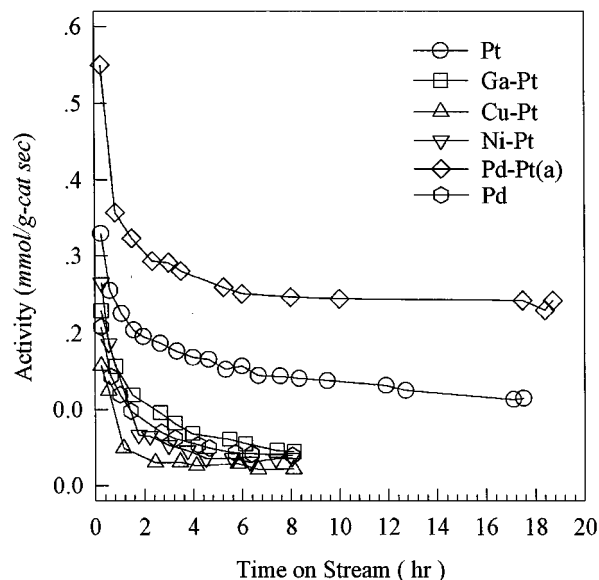**FIG. 2.** Activities of Pt, Pd, and M-Pt/H-Beta catalysts for the conversion of *n*-hexane feed containing 500 ppmw sulfur at 280°C (WHSV = 6.59 h^{-1}, H$_2$/*n*-hexane = 6.0).

Sulfur Tolerance of Various M-Pt/H-Beta Catalysts

To determine their sulfur tolerance, various bimetallic bifunctional M-Pt/H-Beta catalysts were tested for the isomerization of sulfur-containing feed under the same reaction conditions as above. Figure 2 presents the activity changes with the reaction time over Pt/H-Beta, Pd/H-Beta, and various M-Pt/H-Beta catalysts. Among the various second metals, only Pd improved the sulfur tolerance of Pt/H-Beta. Similarly to the study of Ni-Pt/H-mordenite by Jao *et al.* (10), Ni had a negative effect on the sulfur tolerance of Pt/H-Beta. The Pd/H-Beta catalyst was much less sulfur tolerant than Pt/H-Beta, but the bimetallic Pd-Pt/H-Beta series were much more sulfur tolerant than monometallic Pt/H-Beta and Pd/H-Beta.

Table 2 presents the activities of various catalysts and the selectivities to isomers for sulfur-free and sulfur-containing feed. With sulfur-free feed, there was no deactivation with time on stream. The activities of catalysts with sulfur-containing feed were measured at the start (TOS = 15 min) and at the pseudo steady state (TOS = 8 h) of the run. For sulfur-free feed, the activities per gram of catalysts are found to be nearly the same while the TOF values are somewhat different due to the considerable difference in metal dispersion. However, the TOF values are of the same order of magnitude.

Although the activity test for sulfur-free feed was run at much lower WHSV of 1.58 h^{-1}, the selectivity was much higher than that with sulfur-containing feed. The selectivity, as well as the activity, was the highest over Pd-Pt/H-Beta series at steady state of the run with sulfur-containing feed. Second metals other than Pd had a strong negative effect on

TABLE 2

Activity and Selectivity to Isomers for Sulfur-Free and Sulfur-Containing Feed over Pt, Pd, and M-Pt/H-Beta Catalysts

Catalysts	Pt	Pd	Pd-Pt	Ni-Pt	Cu-Pt	Ga-Pt
Nil sulfur[a]						
Activity (mmol/g-cat · h)	15.41	14.88	15.43	15.04	14.94	14.98
TOF (h^{-1})[b]	751.4	1439.6	628.0	2283.5	934.6	1756.1
Selectivity (%)	96.2	95.2	95.5	95.5	94.6	93.7
500 ppmw sulfur[c]						
Activity (mmol/g-cat · h)						
A_I	0.33	0.21	0.55	0.27	0.16	0.23
A_S	0.14	0.04	0.25	0.04	0.02	0.05
A_S/A_I	0.42	0.19	0.45	0.15	0.13	0.22
Selectivity (%) at S. S.	80.0	62.6	87.9	48.7	59.5	64.6

[a] Sulfur-free feed at WHSV $= 1.58$ h^{-1}, H$_2$/n-hexane $= 6.0$.
[b] Turnover frequency obtained from H$_2$ chemisorption (molecules/h · surface metal atom).
[c] Sulfur-containing feed at WHSV $= 6.59$ h^{-1}, H$_2$/n-hexane $= 6.0$. A_I, A_S: Activity (mmol/g-cat · h) at start (at TOS $= 15$ min) and at pseudo steady state (at TOS $= 8$ h) of the run, respectively.

the sulfur tolerance, while their TOF values for sulfur-free feed were larger.

Elemental Analysis

The amounts of sulfur adsorbed (*S atoms/total metal atoms*) and coke deposited on the sulfur deactivated catalysts (wt%) are given in Table 3. The S/M value from Pd-Pt/H-Beta (Pd-Pt(a)) is much less than those from Pt, Pd, and the other M-Pt/H-Beta catalysts. The lower surface coverage of sulfur resulted in reduced coke deposition on Pd-Pt/H-Beta.

The amount of coke deposited on Pd-Pt/H-Beta (0.65 wt%) was about one-third of that on Pt/H-Beta (1.92 wt%), although both catalysts were recovered after the same period of time on stream. Conversely, the H/C atomic ratio from Pd-Pt/H-Beta is about three times larger than that from Pt/H-Beta. Even though Pd and Ni-Pt catalysts were recovered after 8 h of the run, the amounts of coke were observed to be high.

TABLE 3

Elemental Analysis of Sulfur Deactivated Catalysts

Catalysts	Pt[a]	Pd[b]	Pd-Pt[a]	Ni-Pt[b]
Wt%				
C	1.92	0.83	0.65	1.70
H	1.05	0.91	1.07	1.06
S	0.10	0.11	0.06	0.31
Atomic ratio				
H/C	6.54	12.91	19.78	7.46
S/M[c]	0.60	0.36	0.19	0.71

Note. Reaction conditions: WHSV $= 6.59$ h^{-1}, H$_2$/n-hexane $= 6.0$, sulfur content in the feed $= 500$ ppmw S.
[a] Sample recovered after 18 h of the run.
[b] Sample recovered after 8 h of the run.
[c] Sulfur/total metal atomic ratio.

Catalytic Properties of Pd, Pt, and Pd-Pt/H-Beta Catalysts

To get a better insight into the effect of Pd addition on the sulfur tolerance of Pt/H-Beta, the isomerization of pure n-hexane and 500 ppmw sulfur-containing feed was conducted with a larger contact time. i.e., with WHSV $= 1.58$ h^{-1}. The catalytic performance of the Pt, Pd, and Pd-Pt/H-Beta series against sulfur-free and sulfur-containing feed are plotted in Fig. 3. The catalytic performance of Pt, Pd, and Pd-Pt/H-Beta series were about the same for pure n-hexane feed. As shown in Fig. 3, the C$_5^+$ yield, as well as C$_5^+$ selectivity, over all of those catalysts substantially decreased for sulfur-containing feed.

The common features of product distribution caused by the presence of sulfur in the feed over all the catalysts are low catalytic activity and low selectivity to isomers. The catalytic behavior of all the catalysts against sulfur-containing feed is found similar to that of Pt/H-Beta which contains insufficient metal sites. Among the catalysts, Pd/H-Beta was by far the most susceptible to sulfur poisoning. Against sulfur-containing feed, all the Pd-Pt/H-Beta series, irrespective of the preparation methods and the Pd/Pt atomic ratios, showed much improved catalytic performance compared to monometallic Pt/H-Beta and Pd/H-Beta.

Metal Dispersion and Hydrogenation Activities

Bimetallic bifunctional Pd-Pt/H-Beta was found to be more sulfur tolerant than monometallic Pt and Pd/H-Beta for the isomerization of sulfur-containing feed. It is necessary to examine the characteristics of bimetallic Pd-Pt/H-Beta to get a better understanding of the high sulfur tolerance. First, we measured the metal dispersion and the hydrogenation activities of various combinations of Pd and Pt catalysts and the results are given in Table 4.
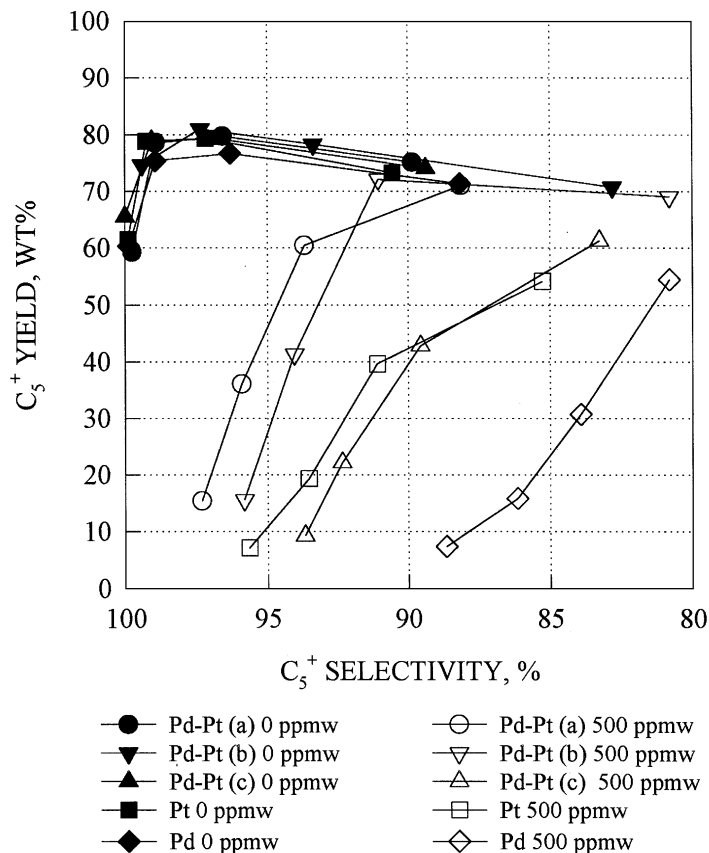
FIG. 3. C_5^+ yield vs C_5^+ selectivity over Pt, Pd, and Pd-Pt series catalysts for pure feed and for sulfur containing feed (WHSV = 1.58 h^{-1}, H$_2$/n-hexane = 6.0).

The total metal sites given in terms of the irreversible hydrogen uptake on Pd and Pd-Pt(c) are lower than those on Pt and Pd-Pt(a). The metal dispersion (H/M) and the hydrogenation activity decreased with increasing Pd portion. The hydrogenation activity of Pd/H-Beta was lower than that of other catalysts by two orders of magnitude whereas the hydrogenation activities of Pt and Pd-Pt(a) given in terms of

TABLE 4

H/M Values and Hydrogenation Activities of Pt, Pd, and Pd-Pt/H-Beta Catalysts

Catalysts	H/M[a]	TOF[b]
Pt	0.40	8.3×10^{-1}
Pd	0.11	5.0×10^{-3}
Pd-Pt(a)	0.25	4.6×10^{-1}
Pd-Pt(c)	0.19	4.9×10^{-1}

Note. Pd-Pt(a): Pd-Pt/H-Beta prepared by IWI with 1.0 wt% of Pt and 0.5 wt% of Pd. Pd-Pt(c): Pd-Pt/H-Beta prepared by IWI with 0.5 wt% of Pt and Pd.

[a] H/total metal atomic ratio obtained from H$_2$ chemisorption.
[b] Turnover frequency for benzene hydrogenation (molecules/sec · surface metal atom).

TOF are in the same order but that of Pt/H-Beta is slightly higher.

H$_2$-TPD

The H$_2$ temperature-programmed desorption profiles from reduced Pt, Pd, and Pd-Pt(a) catalysts are shown in Fig. 4. Two major peaks are observed in each profile; one is at low temperature (LT) and the other at high temperature (HT). The temperature of HT peak from Pd/H-Beta is much higher than that from Pt/H-Beta. The HT peak of Pd-Pt/H-Beta is observed at an intermediate temperature of those from Pt/ and Pd/H-Beta.

In-Situ FT-IR Spectroscopy of CO Adsorbed Catalysts

The infrared spectra of CO adsorbed on Pt, Pd, and Pd-Pt/H-Beta (Pd-Pt(a)) are compared in Fig. 5, showing quite different CO absorption patterns. The intense band at 2087 cm^{-1} and a shoulder at 2121 cm^{-1} were observed for Pt/H-Beta. The intense band at 2087 cm^{-1} was assigned to the linear CO band. According to previous reports, the linear CO band of Pt/H-Beta is observed at much higher wavenumber than that of Pt/alumina (2059 cm^{-1}) (9) and Pt/KL (2000 cm^{-1}) (11, 20). This indicates the existence of strong interaction of Pt clusters with acidic (electron-poor) zeolite Beta. Since no bridging CO band was observed below 2000 cm^{-1}, Pt must have been highly dispersed in zeolites. On the other hand, the linear CO band at 2121 cm^{-1} revealed high thermal stability irrespective of CO coverage, indicating little bimolecular interaction between the adsorbed CO species. The peak location of small
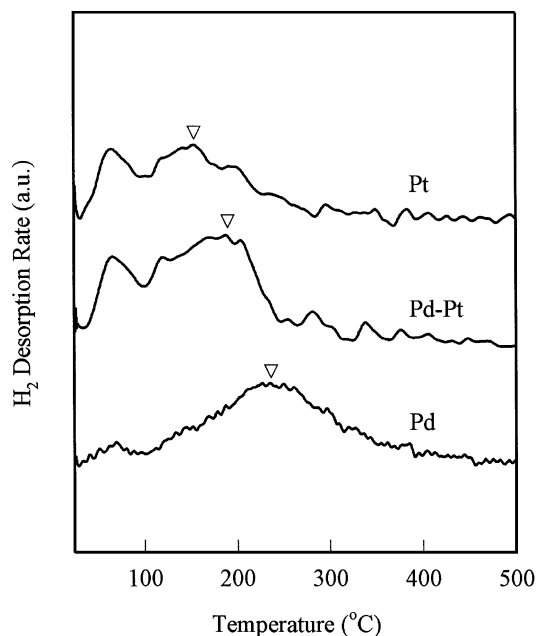

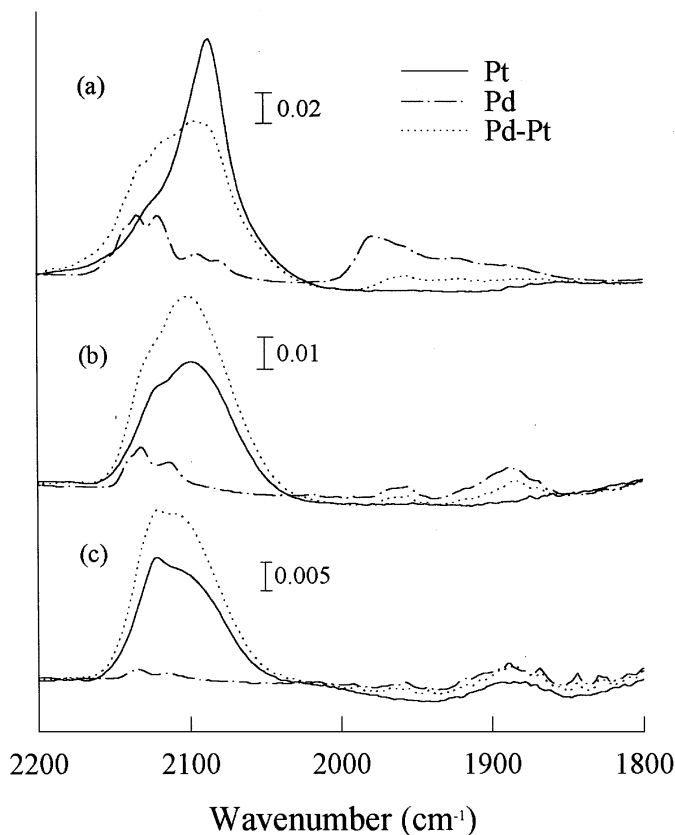**FIG. 4.** H$_2$-TPD profiles from Pt, Pd, and Pd-Pt(a) catalysts.

The CO infrared spectra of Pd-Pt/H-Beta are also given in Fig. 5. The characteristic features here are broadened linear CO band and smaller bridging CO band. In comparison to the case of Pt and Pd/H-Beta, the bands at high wavenumber increased in intensity and the bridging CO band decreased. In Pd-Pt/H-Beta catalyst, however, the bridging CO bands are barely observed.

The infrared spectra of CO adsorbed on Pt, Pd, and Pd-Pt/H-Beta are compared in Fig. 5 after evacuation at different temperatures. The linear CO band on Pt/H-Beta becomes the most intense when evacuated at room temperature, whereas that on Pd-Pt/H-Beta becomes the most intense if it is evacuated at higher temperatures. As shown in Fig. 5c, the band at higher wavenumber (2121 cm^{-1}) is the most intense on Pd-Pt/H-Beta, while it is absent on Pd/H-Beta.

The infrared spectra of CO adsorbed on the bimetallic catalysts are shown in Fig. 6. The bridging CO region is omitted because the bridging CO band is absent on Ni-Pt/H-Beta. The addition of Pd or Ni influenced the spectra in different ways. On the Pd-Pt catalyst, the linear CO band at 2087 cm^{-1} decreased while the band at high wavenumber of 2121 cm^{-1} increased considerably. On the other hand, Ni addition had no significant effect on the spectra of Pt/H-Beta, except for the slight shift of the linear band toward the lower wavenumber. The electron-deficient CO adsorption

FIG. 5. Infrared spectra of CO adsorbed on Pt, Pd, and Pd-Pt/H-Beta after exposure to 20 Torr CO and evacuated at (a) room temperature, (b) 100°C, and (c) 150°C, respectively.

band at 2121 cm^{-1} suggests that this platinum species is in a low positive oxidation state. Kustov *et al.* (21) and Otten *et al.* (22) assigned this peak to CO adsorbed on very small clusters or monatomic Pt^I monocarbonyl species in Pt/H-mordenite. According to Lee *et al.* (23), the intensity of band at 2121 cm^{-1} increased with the calcination temperature and the authors assigned this band to CO adsorbed on very small Pt clusters isolated in the side-pockets of mordenite channel.

As shown in Fig. 5, the IR spectrum of CO adsorbed on Pd/H-Beta is quite complex. In contrast to Pt/H-Beta, a strong absorption band was observed at 1980 cm^{-1} which was assigned to the bridging CO adsorbed on Pd clusters. Other multiple absorption bands are observed between 2160 and 2080 cm^{-1}. According to the literature (24), reduced Pd/alumina sample still contains ionic Pd species (Pd^{2+}, Pd^{1+}) which could give rise to a complex CO absorption pattern from CO adsorbed catalysts. In Pd-loaded zeolites, some Pd clusters might interact with zeolite proton to have electron deficient character as reported by some authors (13, 25–27). These are believed to be responsible for the multiple absorption band of CO adsorbed on Pd/H-Beta catalyst.
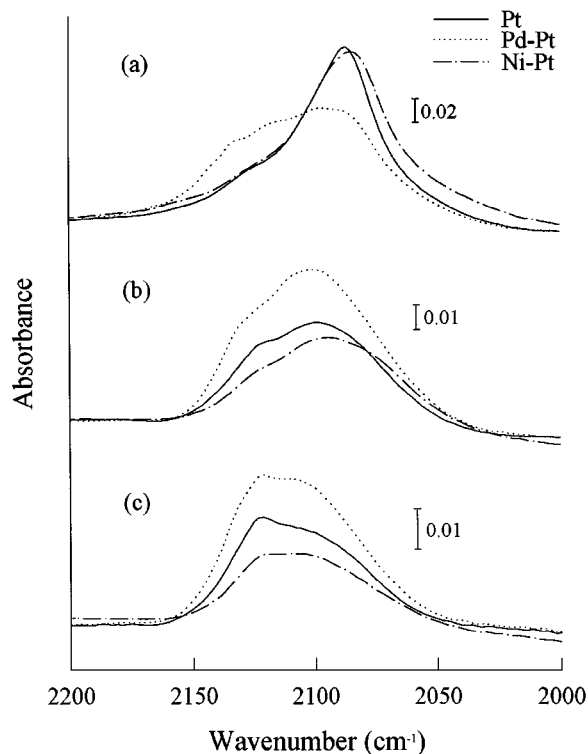

FIG. 6. Infrared spectra of CO adsorbed on Pt, Pd-Pt, and Ni-Pt/H-Beta after exposure to 20 Torr CO and evacuated at (a) room temperature, (b) 100°C, and (c) 150°C, respectively.
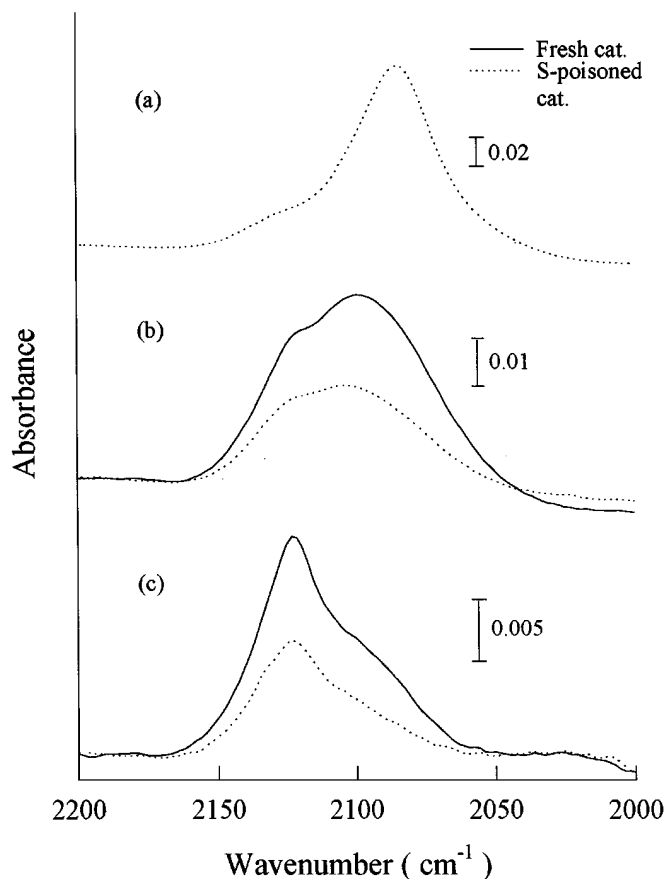
FIG. 7. Infrared spectra of CO adsorbed on fresh and sulfur deactivated Pt/H-Beta after exposure to 20 Torr CO and evacuated at (a) 50°C, (b) 100°C, and (c) 200°C, respectively.

sites observed at 2121 cm^{-1} are the most intense on Pd-Pt catalysts, so the thermal stability of CO is high on Pd-Pt but low on Ni-Pt.

The infrared spectra of CO adsorbed on fresh and sulfur deactivated Pt/H-Beta after evacuation at different temperatures are given in Fig. 7. In comparison to the spectra from fresh Pt/H-Beta catalysts, the spectra from sulfur-deactivated samples show relatively narrow linear CO bands because the intensity of band at 2121 cm^{-1} is reduced. When the evacuation temperature increased, the integrated intensities of linear CO bands at 2087 cm^{-1} and at 2121 cm^{-1} from the sulfur-deactivated sample decreased significantly, compared to those from the fresh samples and this feature becomes more pronounced at higher evacuation temperatures.

DISCUSSION

Irreversible Sulfur Deactivation of Pt/H-Beta Catalyst

Sulfur in the feed causes rapid and significant decrease in catalytic activity of the bifunctional Pt/H-Beta as shown in Fig. 1. The amount of sulfur fed for 15 min with 500 ppmw of sulfur-containing feed corresponds to S/Pt = 0.15. Since the platinum dispersion of Pt/H-Beta is 0.4, this indicates that each sulfur atom poisons 2–3 surface Pt atoms in the bifunctional Pt/H-Beta catalyst, assuming all the S fed is adsorbed.

The accelerated deactivation test with sulfur-containing feed suggests that sulfur deactivation of the bifunctional Pt/H-Beta catalyst for the isomerization of *n*-hexane is an irreversible process. The isomerization of *n*-hexane over Pt/zeolite catalysts is believed to proceed via a bifunctional mechanism involving metal and acid sites (28). When the feed contains sulfur, however, the metal sites are rapidly poisoned by strong sulfur adsorption and then the isomerization seems to proceed via like Friedel–Crafts mechanism in which carbenium ion formation by hydride ion abstraction is the rate-determining step. The carbenium ion formation via a bifunctional mechanism is much faster than via the Friedel–Crafts mechanism (29, 30).

After the metal sites are saturated with sulfur, slow activity loss was observed with reaction time as shown in Fig. 1, which indicates that coke deposition occurs after metal poisoning. Hydrogen reduction of the sulfur deactivated Pt/H-Beta at 500°C restored about 75% of its initial activity. Therefore, the sulfur deactivation of the bifunctional Pt/H-Beta seems to be a two step irreversible process involving metal poisoning by sulfur adsorption, followed by coke deposition on the catalyst.

Characterization of Pd, Pt, and Pd-Pt Catalysts

Among various second metals, only Pd was found to improve the sulfur tolerance of Pt/H-Beta. While monometallic Pd/H-Beta was the most susceptible to sulfur poisoning, the Pd-Pt series showed improved sulfur tolerance. In bimetallic reforming catalysts such as PtSn/KL, PtSn/Al$_2$O$_3$, and PtGe/Al$_2$O$_3$, it has been reported that the sulfur tolerance was improved. However, it was commonly observed that the catalytic activities of bimetallic catalysts for sulfur-free feed were decreased by the addition of second metallic components, compared to the corresponding monometallic Pt catalysts (8, 11). On the other hand, it is evident from our experimental results that Pd addition can improve the sulfur tolerance of the monometallic Pt/H-Beta catalyst without the reduction of its catalytic activity when compared with sulfur-free feed. The different results might have been caused by the different natures of the second metals.

The recent study of bimetallic bifunctional PtPd/Beta by Blomsma *et al.* (31) showed that the bimetallic Pd-Pt zeolite was more active and more selective in the isomerization of *n*-heptane than Pd/H-Beta or Pt/H-Beta. The authors ascribed the higher activity to the improved Pt dispersion by the presence of as little as 20 mol% of palladium, leading to a better proximity and balance of the acid and metal functions. In this study, however, both the metal dispersion (H/M) and the hydrogenation activity

decreased with an increasing Pd portion, in accordance with the results from Rades *et al.* (32). The hydrogenation activity of Pd/H-Beta was lower than that of other catalysts by two orders of magnitude. The total irreversible hydrogen uptakes (μmol/g-cat.) per gram of Pt and Pd-Pt(a) are 10.27 and 12.43 μmol/g-cat., respectively. And the hydrogenation activities of both catalysts given in terms of TOF are in the same order but that of Pt/H-Beta is slightly higher. Therefore, the high sulfur tolerance of Pd-Pt series, compared to monometallic Pt/H-Beta, could not be due entirely to the fact that there are many more metallic sites in Pd-Pt/H-Beta. From these considerations, it is evident that one should take into account the Pd-Pt bimetallic interaction in Pd-Pt series catalysts.

The HT peak of the H_2-TPD profile (Fig. 4) from Pd/H-Beta is observed at a much higher temperature than that from Pt/H-Beta, which suggests that the hydrogenation/dehydrogenation activity of Pd is much lower than that of Pt and this was confirmed by the benzene hydrogenation activity given in Table 4. The HT peak of Pd-Pt/H-Beta is located at an intermediate temperature between those of Pt and Pd/H-Beta, which is a strong indication of Pd-Pt bimetallic interaction in Pd-Pt/H-Beta.

The infrared spectra of CO adsorbed on Pt, Pd, and Pd-Pt/H-Beta are compared in Fig. 5. While only the linear CO band is observed for Pt/H-Beta, an intense bridging CO absorption band is observed at 1980 cm^{-1} for Pd/H-Beta. The CO infrared spectra of Pd-Pt/H-Beta given in Fig. 5a is quite different from those of both monometallic Pd/ and Pt/H-Beta. Compared to the spectra of the monometallic catalysts, the bands at high wavenumber (2121 cm^{-1}) increased in intensity and the bridging CO band was barely observed. Carbon monoxide adsorbs on the Pd surface as bridging the CO but, if the pressure of the CO is increased, some linear species are obtained (33). The decrease in the intensity of the bridging CO implies that the Pd–Pd bond decreased in number by the Pd–Pt bond formation in the Pd-Pt/H-Beta. Carbon monoxide adsorbed on Pd-Pt/H-Beta showed high thermal stability compared to the monometallic Pd and Pt/H-Beta catalysts.

Unlike Pd, Ni had a strong negative effect on the sulfur tolerance of the bifunctional Pt/H-Beta catalyst. Although the TOF of the Ni-Pt/H-Beta catalyst with sulfur-free feed was high, compared to those of the other catalysts as shown in Table 2, the Ni-Pt/H-Beta catalyst was highly susceptible to sulfur poisoning. Ni-Pt interaction in Ni-Pt/H-Beta increased the electron density of Pt and the reduced thermal stability of adsorbed CO as observed from the infrared spectra of CO in Fig. 6. In contrast to our results, the formation of Pt-Ni bimetallic particle in K-LTL made the catalyst more sulfur tolerant than Pt because Ni inhibits sintering at high reaction temperatures (34). However, Ni has an unfavorable effect on the electronic state of Pt under a mild condition like isomerization.

Role of Pd in Pd-Pt/H-Beta Catalysts

The amount of sulfur adsorbed and coke deposited on the sulfur deactivated Pd-Pt/H-Beta catalyst was much lower than those on the monometallic Pd and Pt/H-Beta catalysts. On the other hand, both sulfur adsorption and coke deposition were accelerated on other bimetallic catalysts.

It may be premature to claim that a Pd-Pt alloy was formed in the Pd-Pt/H-Beta catalyst. However, several structural studies concerning Pd-Pt alloy formation are available in the literature (32, 35, 36). Based on their extended X-ray absorption fine structure (EXAFS) study Rades *et al*. (32) reported that randomly mixed particles were formed in Pt-Pd/NaY and the Pt core structure appeared when the Pt content (Pt at% $>$ 75) increased. On the other hand, Hansen *et al*. (36) studied Pt-Pd catalysts supported on HY-zeolite with Pd/Pt atomic ratio greater than unity. From EXAFS study and Monte Carlo simulations, these authors confirmed the surface segregation of palladium. The two different results concerning palladium segregation on the surface (Pt core structure) with respect to the Pd/Pt atomic ratio might have resulted from a large difference in metal loading in two different studies. The Pd-Pt/H-Beta catalyst is different from both catalysts (Pt-Pd/HY and Pt-Pd/NaY) in both metal loading and atomic ratio. From the results of H_2-TPD, H_2-chemisorption, FT-IR spectroscopy of CO-adsorbed catalysts, and the above literature survey, it is evident that a Pd-Pt alloy was formed in Pd-Pt/H-Beta.

As shown in Fig. 7, the integrated intensity of band at 2121 cm^{-1} and the thermal stability of adsorbed CO decreased by sulfur deactivation. The reduced band intensity of a sulfur deactivated sample does not seem to be caused by sintering induced by sulfur because the reaction temperature (280°C) of this study is not so high. On the basis of these results, it is believed that the deactivation of the bifunctional Pt/H-Beta by sulfur is closely related to the decrease in the amount of electron-deficient platinum sites, as noted from Fig. 7.

The coke deactivation of bifunctional Pt/H-zeolite during the conversion of *n*-hexane is caused by the adsorption of olefin intermediates on the acid sites of H-form zeolite. In the case of the sulfur poisoning condition, coke might be deposited on the acid sites near sulfur-adsorbed platinum rather than sulfur-free platinum because sulfur-adsorbed sites lose their metallic function. The sulfur-induced coke deposited on the catalyst could partially neutralize the acid sites and thereby weaken the interaction of Pt clusters with acid sites (electron acceptor) in H-Beta. Strongly bound sulfur could cause a decrease in the electron density of the metal rather than an increase because of the electrophilic nature of the sulfur atom. On the sulfur-deactivated sample, however, electron-deficient metal sites decreased in number. These results are primarily due to sulfur-induced

coking rather than strongly bound sulfur. Therefore, it is reasonable to claim that the decrease in the amount of electron-deficient platinum sites is caused by the reduction of Pt-acidic support interaction which is brought about by sulfur-induced coke. In addition, the strongly bound sulfur on Pt could be another cause of the reduced intensities of linear CO bands at 2121 and 2087 cm^{-1} at high evacuation temperatures.

Consequently, the positive effect of palladium presence in bimetallic bifunctional Pd-Pt/H-Beta on the sulfur tolerance may be attributed to the increase in the amount of electron deficient metal sites which in turn reduces the irreversible electrophilic sulfur adsorption and thereby sulfur-induced coking.

CONCLUSIONS

We have studied the sulfur tolerance of monometallic Pt/H-Beta and Pd/H-Beta and various bimetallic M-Pt/H-Beta catalysts (M = Pd, Ni, Cu, and Ga) for the isomerization of *n*-hexane. Sulfur in the feed gave rise to a significant loss of catalytic performance and the sulfur deactivation of bifunctional Pt/H-Beta turned out to be a two step irreversible process caused by metal poisoning followed by coking.

Among various second metals employed in this study, only Pd improved the sulfur tolerance of Pt/H-Beta and the other metals showed a strong negative effect. With sulfur-free feed, the monometallic Pt/H-Beta and Pd/H-Beta showed similar activity and isomer selectivity to bimetallic Pd-Pt series. When the feed contained sulfur, however, the Pd-Pt series showed higher sulfur tolerance than Pd/H-Beta and Pt/H-Beta, regardless of the preparation method and the Pd/Pt atomic ratio. Both the metal dispersion and the hydrogenation activity were decreased by Pd addition. However, the Pd-Pt bimetallic interaction brought about the increase in the amount of electron-deficient metal sites, which improved the sulfur tolerance by reducing irreversible electrophilic sulfur adsorption and thereby reducing sulfur-induced coke formation.

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