Hydrogenation of tetralin over zeolite-supported Pd–Pt catalysts in the presence of dibenzothiophene

Hiroyuki Yasuda * and Yuji Yoshimura

National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan
E-mail: yasuda@nimc.go.jp

Received 7 November 1996; accepted 26 March 1997

The sulfur tolerance of Pd–Pt bimetallic catalysts supported on various zeolites was investigated for the hydrogenation of tetralin. The reaction was carried out at a hydrogen pressure of 3.9 MPa at 553 K in the presence of dibenzothiophene at a sulfur concentration of 500 wtppm. The coexistence of Pt with Pd on USY zeolite ($SiO_2/Al_2O_3 = 680$) greatly enhanced the tetralin hydrogenation activity and improved the sulfur tolerance, which depended on the Pd/Pt ratio and reached a maximum at a Pd : Pt mole ratio of 4 : 1. The influence of the support material, such as USY zeolite ($SiO_2/Al_2O_3 = 15.0$), HY zeolite, HL zeolite, and H-mordenite, on the hydrogenation activity and selectivity and on the sulfur tolerance, was also investigated for the bimetallic Pd–Pt(4 : 1) catalyst. For maximizing the hydrogenation selectivity while minimizing the yield of cracked products and gases, the Pd–Pt(4 : 1) catalyst on USY zeolite ($SiO_2/Al_2O_3 = 680$) was more effective than Pd–Pt on the other supports, although its sulfur tolerance was lower.

Keywords: hydrogenation of tetralin, USY zeolite, palladium, platinum, sulfur tolerance

1. Introduction

Removal of aromatic compounds in diesel fuel has received considerable attention [1–3] because such compounds have been recognized as precursors of particulates in the exhaust gases from diesel engines. In addition, a high aromatic content lowers the quality of diesel fuel, such as cetane number, smoke point, and coloring. Strict regulations limiting the aromatic content have already been introduced in Sweden and in California (USA). Under such regulations, the development of catalytic technology for deep aromatic saturation is much needed. One group of candidates for the catalyst in the hydrogenation of aromatics consists of conventional hydrotreating catalysts, such as sulfided Ni–Mo and Ni–W on Al_2O_3. Such catalysts have the advantage of high tolerance to sulfur in the feedstock. However, the activity of a metal sulfide catalyst is not sufficient, so severe operating conditions, such as high hydrogen pressure and high temperature, are required. But high temperature is thermodynamically unfavorable for the hydrogenation of aromatics. Another group of candidates is formed by noble metal catalysts. For these catalysts, the content of sulfur in the feedstock must be strictly reduced before the catalyst comes in contact with the feedstock, because noble metals are generally poisoned easily by even a few parts per million of sulfur in the feedstock [4,5]

Recently, much attention has been paid to high sulfur tolerance of Pd, Pt, or their mixtures supported on Al_2O_3, TiO_2, or acidic zeolite for the hydrogenation of aromatics [6–12]. In this study, we chose the hydrogenation of tetrahydronaphthalene (tetralin) in the presence of dibenzothiophene (DBT) as a model reaction. We then attempted to clarify the effect of the Pd/Pt ratio on the sulfur tolerance of Pd–Pt bimetallic catalysts supported on USY zeolite. We also studied the influence of the type of zeolite on the hydrogenation activity and selectivity and on the sulfur tolerance.

2. Experimental

2.1. Catalyst preparation and characterization

USY zeolite ($SiO_2/Al_2O_3 = 15.0$), hereafter called HY-15.0, H-mordenite ($SiO_2/Al_2O_3 = 23.0$), and HL ($SiO_2/Al_2O_3 = 6.1$) zeolite were obtained from Tosoh Co. and used as received. HY zeolite was prepared from NaY zeolite supplied by Catalysts and Chemicals Industries Co. NaY was ion-exchanged using an aqueous solution of ammonium nitrate at 298 K for 24 h, filtered, and then washed with deionized and distilled water. This procedure was repeated three times. The ion-exchanged zeolite was then dried at 383 K overnight and calcined at 773 K for 2 h. The SiO_2/Al_2O_3 ratio of HY determined using ICP measurements was 5.1; we called this zeolite, HY-5.1. HY-15.0 was further dealuminated by extraction with hydrochloric acid (2.0 mol dm^{-3}) at 373 K for 2 h. After the extraction, the zeolite was filtered, washed with water until no chloride ions were detected in the fresh filtrate, and then dried at 383 K

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* To whom correspondence should be addressed.

overnight. The SiO_2/Al_2O_3 ratio of zeolite thus obtained was 680; we called this zeolite, HY-680.

The monometallic (Pd, Pt) and bimetallic (Pd–Pt) catalysts supported on zeolites were prepared by incipient wetness impregnation with either an aqueous solution or a mixed aqueous solution containing appropriate amounts of $[Pd(NH_3)_4]Cl_2$ and $[Pt(NH_3)_4]Cl_2$. The total metal content of each catalyst was 1.2–1.3 wt%. The impregnated samples were dried in vacuum at 333 K for 6 h, pressed into a wafer, crushed into 22/48 mesh chips, and then stored in a desiccator. The sample was calcined in an oxygen stream (2 $dm^3\ min^{-1}\ g^{-1}$) at 573 K for 3 h at a heating rate of 0.5 K min^{-1} before being used in the reaction and the measurement of the metal dispersion.

Adsorption of CO was measured using a pulse method to determine the dispersion of Pd, Pt, and Pd–Pt supported on zeolites. The stoichiometry of CO to either Pd or Pt was assumed to be unity [13,14]. About 50 mg of precalcined sample was treated in a hydrogen stream (30 $cm^3\ min^{-1}$) at 573 K for 1 h, purged by helium at the same temperature for 10 min, and cooled to room temperature. After the pretreatment, pulses of CO (9.8 vol%) in helium were injected into the sample several times at room temperature. The volume of each pulse was 0.5 cm^3. The amount of CO uptake was measured by a thermal conductivity detector. Two measurements were taken for each catalyst, and the average was adopted.

2.2. *Catalytic testing*

The hydrogenation of tetralin was carried out in a high-pressure fixed-bed continuous-flow reactor, which was operated in the up-flow mode. The reactor was a 316 stainless-steel tube (1/6 in. i.d. and 0.6 m long). For reproducible reaction data, each catalytic test was carried out with a new reactor tube. The reactor was covered with a bronze isothermal jacket (0.4 m long) whose temperature was controlled by an electric furnace. The temperature of the catalyst bed was thus maintained isothermally. The top part of the catalyst bed was in contact with a thermo-well (1/8 in. o.d., 316 stainless-steel) into which a thermocouple was inserted to measure the reaction temperature. The bottom part of the catalyst bed was filled with stainless-steel beads (2 mm o.d.), which acted as a preheating zone. The hydrogen flow rate was controlled by a mass flow controller. The liquid feed, which contained tetralin (30 wt%), DBT (0.3 wt%, sulfur concentration of 500 wtppm), and *n*-hexadecane (for balance), was supplied by a liquid chromatographic pump at a rate that was monitored using an electric balance on which a feed tank was placed. The standard experimental conditions were a total pressure of 3.9 MPa, reaction temperature of 553 K, feed flow rate of 4 g h^{-1}, hydrogen flow rate of 2.46 $dm^3\ h^{-1}$, catalyst weight of 0.25 to 0.5 g, and weight hourly space velocity (WHSV) of 8 to 16 h^{-1}. The volume ratio of hydrogen (gas NTP) to feed (liquid) was 500. Prior to catalytic testing, the precalcined sample was reduced in situ by exposing it to a hydrogen stream (100 $cm^3\ min^{-1}$) at 101.3 kPa while increasing the temperature from room temperature to 573 K (at an increase of 0.5 K min^{-1}) and then kept at 573 K for 3 h. After this reduction, the catalyst temperature was lowered to 553 K and the reactor was pressurized with hydrogen. The feed was then mixed with hydrogen and introduced into the preheating zone. The liquid products of the reaction were periodically collected, and then analyzed using a Shimadzu GC-9A gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard Ultra 1 (0.2 mm i.d. and 50 m long) capillary column.

3. Results and discussion

3.1. *Kinetics of tetralin hydrogenation over the Pd–Pt/HY-5.1 catalyst*

The hydrogenation of tetralin over the Pd–Pt bimetallic catalyst (Pd : Pt mole ratio of 4 : 1, hereafter abbreviated as Pd–Pt(4 : 1)) supported on HY-5.1 was carried out in the WHSV range from 5.6 to 16 h^{-1}. Figure 1 shows the time course of the conversion of tetralin into decalins (the sum of cis- and trans-decahydronaphthalene). The conversions decreased with time and reached a constant after the time on stream (*t*) exceeded 24 h. During the hydrogenation reaction, the major products were cis- and trans-decalin, and the minor products, which were produced via isomerization and hydrocracking reactions, were decalin isomers ($C_{10}H_{18}$ compounds, such as methylbicyclo[0.3.4]nonanes and dimethylbicyclo[0.3.3]octanes), alkylcyclohexanes, alkylcyclopen-

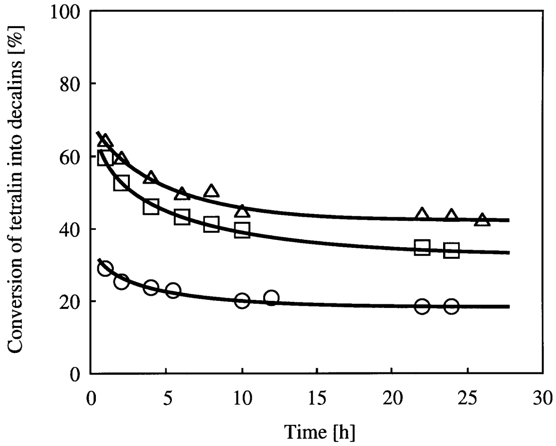

Figure 1. Time course of the conversion of tetralin into decalins (the sum of cis- and trans-decalin) for the hydrogenation of tetralin in the presence of DBT (sulfur concentration of 500 wtppm) over the Pd–Pt(4 : 1)/HY-5.1 catalyst. Reaction conditions: 553 K; hydrogen pressure of 3.9 MPa; feed flow-rate of 4 g h^{-1}; WHSV of 16 h^{-1} (○), 8 h^{-1} (□), and 5.6 h^{-1} (△).

tanes, alkylbenzenes, paraffins, and gases. The reaction selectivity to decalins was over 80% in this catalyst, and little change in the hydrogenation selectivity was observed between the initial period ($t = 4$ h) and the final period ($t = 24$ h). The conversion of DBT reached 100%.

Figure 2 shows a linear relationship between the ln $[1/(1 - X)]$ values and the 1/WHSV values, where X is the conversion of tetralin into decalins at $t = 24$ h. This relationship indicates that the kinetics of the tetralin hydrogenation over the Pd–Pt(4 : 1)/HY-5.1 catalyst was first-order in tetralin content. We therefore evaluated the hydrogenation activity using a first-order rate constant per exposed surface metal atom defined as:

$$k = \ln[1/(1 - X)]\, F/(MWN),$$

where X is the conversion of tetralin into decalins, F is the flow rate of the liquid feed (g h^{-1}), M is the molecular weight of the feed (186.4 g mol^{-1}), W is the weight of catalyst (g), and N is the number of exposed surface metal atoms per weight of catalyst (mol g^{-1}) obtained by CO adsorption.

For evaluating the effect of the film mass transfer on the catalytic performance of Pd–Pt(4 : 1)/HY-5.1, we measured the hydrogenation rate constant for various levels of F (from 2 to 5.8 g h^{-1}) and W (from 0.25 to 0.72 g) at a constant WHSV (8 h^{-1}) and a constant hydrogen/feed ratio (500). The hydrogenation rate constant did not change at all (figure 2). Therefore, for the standard experimental conditions ($F = 4$ g h^{-1}, $W = 0.25$–0.5 g, and WHSV = 8–16 h^{-1}), the film resistance was negligible. Next, for evaluating the effect of the pore diffusion on the catalytic performance, the hydrogenation rates for different catalyst particle sizes were measured. The conversion of tetralin into decalins at WHSV = 8 h^{-1} was 33.9% for a 22/48 mesh size (standard) and 41.1% for a 36/80 mesh size, respectively (figure 2). The effectiveness factor for the 22/48 mesh size catalyst was calculated as 0.69 [15]. However, we carried out a series of reaction tests using a 22/48 mesh size catalyst in order to avoid a significant pressure drop, although the reaction rate was influenced by the pore diffusional resistance.

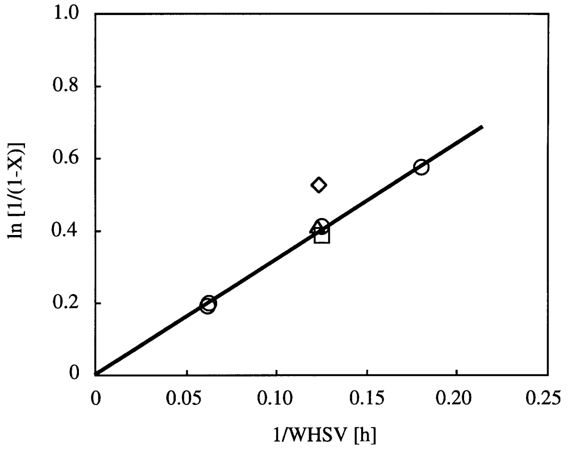

Figure 2. First-order kinetic plot for the hydrogenation of tetralin in the presence of DBT over the Pd–Pt(4 : 1)/HY-5.1 catalyst for a 22/48 mesh size and a feed flow-rate of 2 g h^{-1} (△), 4 g h^{-1} (○), and 5.8 g h^{-1} (□), and for a 36/80 mesh size and a feed flow-rate of 4 g h^{-1} (◇). Here, X is the conversion of tetralin into decalins.

3.2. Catalytic activity of Pd–Pt on HY-680 zeolite

The effect of the Pd/Pt ratio on the tetralin hydrogenation activity and the sulfur tolerance of the Pd–Pt/HY-680 catalysts was examined. Figure 3 shows the time course of the activity (k_S) for the Pd/HY-680, Pt/HY-680, and Pd–Pt(4 : 1)/HY-680 catalysts (at WHSV = 16 h^{-1}). The products derived from tetralin were only cis- and trans-decalin, and the selectivity of decalins was almost 100%. In other words, the isomerization or hydrocracking of tetralin and decalins hardly occurred. This is because the amount of acid in the support was very small (the SiO_2/Al_2O_3 ratio was 680) and the reaction temperature was low (553 K). The conversion of DBT for the Pd–Pt/HY-680 and Pt/HY-680 catalysts was 100% at $t = 24$ h, while that for Pd/HY-680 was 54%. For comparison, also shown in figure 3 is the time course of the activity (k) for the Pd–Pt(4 : 1)/HY-680 catalyst measured at WHSV = 400 h^{-1} and in the absence of DBT. When DBT was present, the activity significantly decreased with time, and reached a constant after $t = 24$ h. On the other hand, when DBT was not present, the activity was much higher and no deactivation was observed, even after 24 h. This means that the deactivation was due to the poisoning of the metals by sulfur, and that the influence of coke deposition or agglomeration of metals on the deactivation was small. As shown in figure 3, when DBT was present, the coexis-

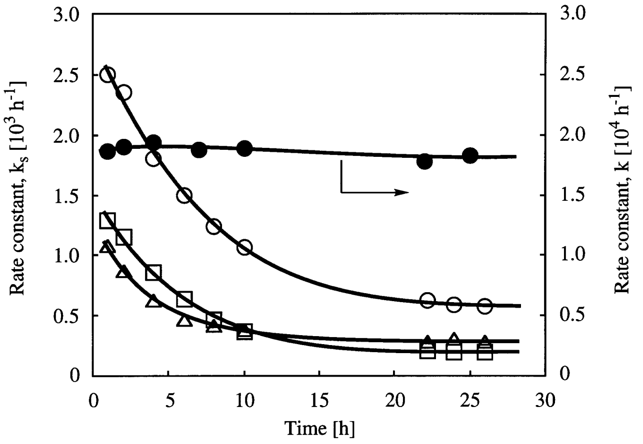

Figure 3. Time course of the tetralin hydrogenation activity for the Pd–Pt(4 : 1)/HY-680 (○), Pd/HY-680 (□), and Pt/HY-680 (△) catalysts in the presence of DBT (sulfur concentration of 500 wtppm) and for the Pd–Pt(4:1)/HY-680 (●) catalyst in the absence of DBT. Reaction conditions were 553 K and a hydrogen pressure of 3.9 MPa.

Table 1
Tetralin hydrogenation activity of Pd–Pt catalysts supported on HY-680 [a]

Metal [b]	Atomic ratio	Dispersion	Rate constant		k_s/k	RA [e]
			k_s [c] (10^2 h^{-1})	k [d] (10^4 h^{-1})		
Pd		0.57	2.0	1.0	0.020	0.15
Pd–Pt	9 : 1	0.59	3.2	–	–	0.18
Pd–Pt	4 : 1	0.43	5.9	1.8	0.032	0.24
Pd–Pt	3 : 2	0.53	3.9	1.8	0.022	0.20
Pd–Pt	3 : 7	0.55	2.9	–	–	0.20
Pt		0.43	3.0	2.6	0.012	0.28

[a] Reaction conditions: 553 K; hydrogen pressure of 3.9 MPa; WHSV of 16 h^{-1} (in the presence of DBT (sulfur concentration of 500 wtppm)) and 400 h^{-1} (in the absence of DBT); time on stream (t) of 24 h.

[b] Total amount of metal loading was 1.2–1.3 wt%.

[c] k_s: rate constant in the presence of DBT.

[d] k: rate constant in the absence of DBT.

[e] RA: the ratio of k_s at $t = 24$ h to k_s at $t = 1$ h.

tence of Pt with Pd improved the sulfur tolerance and greatly enhanced the activity.

Table 1 lists the hydrogenation rate constants in the presence of DBT (k_s) and in the absence of DBT (k) at $t = 24$ h, and the metal dispersion for the Pd–Pt/HY-680 catalysts. The k_s/k ratio at $t = 24$ h and the relative activity (RA), which was defined as the ratio of k_s at $t = 24$ h to k_s at $t = 1$ h, are also listed to evaluate the catalyst deactivation. Figure 4 shows the values of k_s and k at $t = 24$ h versus the mole ratio of Pt. In the presence of DBT, a remarkable synergistic effect was observed between Pd and Pt: the activity increased with the increase in Pt content, reached a maximum when the Pd : Pt mole ratio was 4 : 1, and decreased with further increase in Pt content. The combination of Pd and Pt supported on Al_2O_3 or various zeolites was previously shown to be effective for the hydrogenation of aromatics in petroleum feedstocks containing sulfur compounds [6–8]. Though the SiO_2/Al_2O_3 ratio of USY zeolite used in this study is quite different from that of zeolites reported in the literature [7], we confirmed the synergism between Pd and Pt for the hydrogenation of tetralin in the presence of DBT. In contrast, the activity obtained at the sulfur-free condition was much higher than that obtained in the presence of DBT. Furthermore, the activity generally increased with the increase in Pt content.

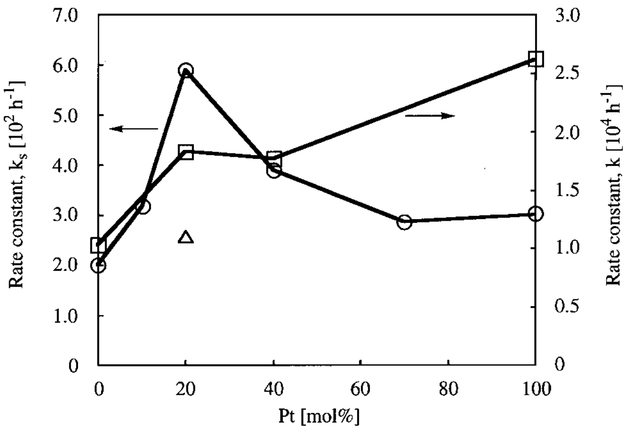

Figure 4. Effect of the Pd/Pt ratio on the activity for the hydrogenation of tetralin over Pd–Pt/HY-680 catalysts in the presence of DBT (○) and in the absence of DBT (□) and over a physical mixture of Pd/HY-680 and Pt/HY-680 with Pd : Pt = 4 : 1 in the presence of DBT (△). Reaction conditions: 553 K; hydrogen pressure of 3.9 MPa; time on stream (t) of 24 h.

As shown in table 1, the k_s/k ratio peaked at Pd : Pt = 4 : 1. This suggests that the highest activity of Pd–Pt(4 : 1)/HY-680 catalyst in the presence of DBT is due to the highest sulfur tolerance among the Pd–Pt/HY-680 catalysts. Consequently, the high activity was maintained for the Pd–Pt(4 : 1)/HY-680 catalyst even after 24 h, as shown by RA in table 1. It is known that the dispersion of metal is an important factor in controlling the sulfur tolerance [4]. In our results, however, the high sulfur tolerance was not correlated with the degree of the metal dispersion, because the metal dispersion differed only slightly among the Pd–Pt/HY-680 catalysts. The specific structure or electronic state of Pd and Pt at around Pd : Pt = 4 : 1 is therefore rather important for the high sulfur tolerance.

The activity of a physical mixture of Pd/HY-680 and Pt/HY-680 with a Pd : Pt mole ratio of 4 : 1 and a total amount of metal loading of 1.2 wt% is also shown in figure 4. The activity was lower than that for the Pd–Pt(4 : 1)/HY-680 catalyst prepared using a co-impregnation method. Furthermore, no synergistic effect of Pd and Pt was observed. The results show that the presence of Pd and Pt at Pd : Pt = 4 : 1 either in the neighborhood of each other or as an alloy plays a significant role in high sulfur tolerance. Note that Pd and Pt form an alloy structure at Pd : Pt = 4 : 1 [16,17]. We are currently investigating the supported structure of Pd and Pt.

3.3. *Comparison of various zeolite supports for Pd–Pt catalysts*

The activity and the sulfur tolerance of Pd–Pt cat-

Table 2
Tetralin hydrogenation activity and selectivity of Pd–Pt(4 : 1) catalysts supported on various zeolites in the presence of DBT (sulfur concentration of 500 wtppm) [a]

Catalyst [b]	Dispersion	Conversion of tetralin (%)	Selectivity [c] (%)		Rate constant k_s (10^2 h^{-1})	RA [d]
			decalins [e]	decalin isomers [f]		
Pd–Pt/HY-680	0.43	25.7 [g]	99.7	nd [i]	5.9	0.24
Pd–Pt/HY-15.0	0.34	56.4 [g]	68.2	15.2	12.7	0.50
Pd–Pt/HY-5.1	0.19	22.5 [g]	81.3	13.4	9.0	0.59
Pd–Pt/HL	0.33	16.5 [h]	66.5	24.1	1.5	0.50
Pd–Pt/H-mordenite	0.66	7.5 [h]	20.6	36.8	0.1	0.36

[a] Reaction conditions: 553 K; hydrogen pressure of 3.9 MPa; time on stream (t) of 24 h.

[b] Total amount of metal loading was 1.2–1.3 wt%.

[c] Selectivity of products other than decalins and decalin isomers (i.e. 100% − (decalins (%) + decalin isomers (%)) was attributed to the formation of alkylcyclohexanes, alkylcyclopentanes, alkylbenzenes, paraffins, and gases.

[d] RA: the ratio of k_s at $t = 24$ h to k_s at $t = 1$ h. [e] The sum of cis- and trans-decalin.

[f] See section 3.1. [g] WHSV= 16 h^{-1}. [h] WHSV = 8 h^{-1}. [i] Not detected.

alysts supported on various zeolites were compared. The atomic ratio of Pd to Pt was fixed at 4, because a maximum activity was obtained at Pd : Pt = 4 : 1 (table 1 and figure 4). Except for HY-680, all the zeolite supports allowed isomerization and hydrocracking as well as hydrogenation to proceed. The products other than decalins were discussed in section 3.1. Table 2 summarizes the dispersion, the selectivity of decalins (the sum of cis- and trans-decalin) and decalin isomers at $t = 24$ h, the rate constant (k_s) at $t = 24$ h, and the relative activity (RA). Note that the selectivity for all the catalysts only weakly depended on the conversion of tetralin.

As shown in table 2, the hydrogenation activity (k_s) was highest for Pd–Pt/HY-15.0, followed by HY-5.1, HY-680, HL, and H-mordenite. Song et al. [12] reported that Pd or Pt supported on H-mordenite ($SiO_2/Al_2O_3 = 38$) is more active than Pd or Pt on HY zeolite for the hydrogenation of naphthalene in the presence of benzothiophene. The difference may be due to the kind of metal, the properties of the support (e.g., surface area and acidity), and the reaction conditions. Note that for the reactions, Song et al. used a batch reactor, a lower sulfur-to-metal ratio (S/metal) of about 4, and a shorter reaction period of 2 h, whereas the S/metal ratio in this study was about 30 after a time on stream of 24 h. The selectivity of decalins for the Pd–Pt/HY-680 catalyst (table 2) was extremely high and reached almost 100%, as mentioned in section 3.2. In contrast, Pd–Pt/H-mordenite, which has a strong acid site, showed a high hydrocracking activity and a low selectivity of hydrogenation.

The relative activity was highest for the Pd–Pt/HY-5.1 catalyst, followed by HY-15.0 and HL. On the other hand, the deactivation for Pd–Pt/HY-680 was higher than even that for Pd–Pt/H-mordenite. The acidic protons on a support reduce the electron density of a supported metal, and as a result weaken the bonding energy between the metal and sulfur [18,19]. Therefore, the acidity of HY-5.1 and HY-15.0 probably enhanced the sulfur tolerance of Pd–Pt. It is suggested by the lower selectivity of decalins with these supports compared with HY-680. In contrast, because the amount of acid in HY-680 was extremely small, Pd–Pt on HY-680 was easily poisoned by sulfur, and thus increased the deactivation. However, for maximizing the hydrogenation selectivity while minimizing the yield of cracked products and gases, the Pd–Pt/HY-680 catalyst was more effective than Pd–Pt on HY-15.0 and HY-5.1.

4. Conclusions

– The coexistence of Pt with Pd on USY zeolite ($SiO_2/Al_2O_3 = 680$) resulted in an increase in the steady-state activity for the hydrogenation of tetralin in the presence of DBT (sulfur concentration of 500 wtppm). The activity and the sulfur tolerance of the Pd–Pt catalysts depended on the Pd/Pt ratio and reached a maximum at a Pd : Pt mole ratio of 4 : 1. The high sulfur tolerance of Pd–Pt(4 : 1) may be due to the structural and electronic effects rather than to the degree of the metal dispersion.

– For maximizing the hydrogenation selectivity while minimizing the yield of cracked products and gases, the Pd–Pt(4 : 1) catalyst on USY zeolite ($SiO_2/Al_2O_3 = 680$) was more effective than Pd–Pt on either USY zeolite ($SiO_2/Al_2O_3 = 15.0$), HY zeolite, HL zeolite, or H-mordenite, although the sulfur tolerance of Pd–Pt on USY zeolite ($SiO_2/Al_2O_3 = 680$) was relatively lower.

Acknowledgement

We thank Dr. Y. Sugimoto of the National Institute of Materials and Chemical Research for the measurement of GC-MS and for helpful discussion. We also thank Catalysts and Chemicals Industries Co. for the ICP measurements.

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