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Noble metal catalysts for low-temperature naphthalene hydrogenation in the presence of benzothiophene

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Abstract

Pt/Al_2O_3, Pd/Al_2O_3, and Pd/TiO_2 catalysts were compared to a commercial hydrotreating catalyst, $NiMo/Al_2O_3$, for naphthalene hydrogenation inside tubing bombs at 553 K with a cold feed (at room temperature) of 6.99 MPa H_2 and tridecane as the solvent. The noble metal catalysts were found to be significantly more active than $NiMo/Al_2O_3$. A further study at a reaction temperature of 473 K showed that naphthalene hydrogenation over these noble metal catalysts can proceed even in the presence of benzothiophene at a concentration of 4200 ppm. Sulfur addition does decrease the activity of all the noble metal catalysts. However, Pd catalysts appear to have higher sulfur resistance than the Pt catalyst; Pd/TiO_2 catalyst was found to be the most active and the least affected by benzothiophene among the three noble metal catalysts studied.

Keywords: Naphthalene hydrogenation; Benzothiophene; Noble metal catalysts

1. Introduction

Recently, due to the more and more stringent environmental regulations and fuel specifications, reduction of aromatics in distillate fuels such as diesel fuel, gasoline and jet fuel has received considerable attention. Conventional hydrotreating processes are currently used in industry for aromatic saturation [1]. Hydrogenation and partial hydrogenation of aromatic compounds are also important for producing solvents and advanced liquid fuels. This work is a part of our effort in an on-going program to develop advanced thermally stable jet fuels from coal-derived liquids and petroleum, where both complete and partial hydrogenation reactions of naphthalene-type compounds have important roles to play. Complete saturation of naphthalene gives decalins which show much higher thermal stability than long-chain alkanes, while partial saturation produces tetralin which can substantially inhibit the thermal degradation and solid-forming tendency of long-chain alkanes in jet fuels at high temperature [2–4].

The hydrogenation of aromatic and polycyclic aromatic compounds are typically exothermic [1,5]; therefore, a lower reaction temperature is thermodynamically favorable. However, in hydrotreating fuels and heavy liquids where polycyclic aromatic compounds are present, a reaction temperature above 623 K is typical in conventional processes which conse-

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quently requires a high concentration of hydrogen to offset the limitation of thermodynamic equilibrium conversion. Noble metal catalysts are active for the hydrogenation of aromatics even at a temperature below 473 K [1,6,7], but they were not used for hydrotreating owing to cost and susceptibility to the poisoning by sulfur-containing compounds [8]. However, recent studies showed that some noble metal catalysts may not be as sensitive to sulfur as had been generally recognized [9–13]. This study attempted to examine the potential of using noble metal catalysts for low-temperature hydrotreating reactions in the presence of sulfur-containing compounds. As a model reaction, naphthalene hydrogenation was conducted in the absence and presence of benzothiophene.

2. Experimental

2.1. Catalyst preparation

Pt/Al_2O_3, Pd/Al_2O_3, and Pd/TiO_2 catalysts were all prepared by incipient wetness method using H_2PtCl_6 (Aldrich, 99.995%) and $PdCl_2$ (Aldrich, 99.995%; dissolved in ultra pure HCl solution before use) as the precursors. The pore volume and surface area of the support are 0.8 cc/g and 200 m^2/g for γ-Al_2O_3 (Sumitomo Metal Mining, S-1, ground to 80–120 mesh size) [14] and 0.5 cc/g and 50 m^2/g for TiO_2 (Degussa, P25), respectively. The supports were calcined at 773 K under dry air flow for 2 h before use. A nominal loading of 2 wt% metal was used for all three catalysts. A commercially available hydrotreating catalyst $NiMo/Al_2O_3$ (P-modified and presulfided) [15] was used as the reference without further pretreatment. The pretreatment of the noble metal catalysts was carried out in a flow-type glass reactor having a side arm connection to a catalyst transfer tube such that the pretreated catalyst powders can be poured into the transfer tube without exposing to the air. The transfer tube loaded with pretreated catalyst was stored under N_2 in a custom-made glove box. The pretreatment conditions for these noble metal catalysts were H_2 reduction at 723 K for Pt/Al_2O_3, 20% O_2 calcination at 673 K for Pd/Al_2O_3, and H_2 reduction at 473 K for Pd/TiO_2; these conditions were found to give relatively higher activities for naphthalene hydrogenation at 553 K with these three noble metal catalysts [16].

2.2. Reaction conditions

Hydrogenation was carried out using tubing bombs made from a pair of welded connectors (Swagelok, ss316) and a 1/4″ tube side arm for connection to a pressure gauge and a close-off valve. The total inner volume of the bomb is approximately 25 ml. Bombs were typically loaded with 4 g tridecane (Aldrich, 99%), 1 g naphthalene (Fischer, certified grade), and in certain cases, 9 mg or 21 mg of benzothiophene (Fluka, 99%). Loading of the pretreated catalyst was performed under a N_2 environment in a home-made glove box, where the bomb was subsequently sealed. Thereafter, the bomb was connected to a gas manifold via its side-arm and the atmosphere inside the bomb was replaced by H_2 (MG Ind., 99.999%) using dilution purge, i.e. at least 8 cycles of pressurizing with H_2 to 6.99 MPa followed by a careful venting to approximately 0.45 MPa. At the completion of dilution purge, the bomb was charged with H_2 to either 6.99 or 10.44 MPa, disconnected from the manifold, plunged into a fluidized sandbath (Tecam) preset to the desired reaction temperature, and the reaction was timed. The reaction temperature was typically controlled to an accuracy of 10 K. After the reaction, the bomb was removed from the sandbath and quenched in a cold water bath.

On cooling, the pressure in the tubing bomb was carefully released to prevent any entrainment of liquid in the vent gas; part of the vent gas was collected in a gas bag for composition analysis. The bomb was then opened and the liquid content was poured into a funnel with filter paper, followed by rinsing and flushing the bomb with acetone (Aldrich, 99.9%); the filtrate and the wash solution were separately stored in small vials for later analysis. The solid residue on the filter paper was dried in an oven at 393 K for at least 3 h and then weighed.

2.3. Product analysis

The composition of the vent gas was analyzed by GC (Perkin-Elmer 5800) using a Chemipack C18 (Alltech, 1/8″, 6 ft) column with FID and Carboxene 1000 (Supelco, 1/8″, 15 ft) column with TCD. The gas yield and the amount of H_2 reacted were calculated from the average molecular weight of the vent gas, the bomb pressure after reaction, and the weight change before and after the bomb was vented; details of the calculation are given in the Appendix. Liquid samples were analyzed quantitatively by GC (HP5890II) analysis with *n*-nonane (Aldrich, 99.9%) as the internal standard using either a DB-17 (J&W, 30 mx0.25 mm) or a Rtx-50 (Restek, 30 mx0.25 mm) capillary column with a FID detector. The response factors of individual species were determined by injection of mixtures of known composition. GC–MS (HP5890II GC coupled with a HP5971A MSD) equipped with the same type of capillary column was used to identify the compositions in the liquid products from time to time. The sum of the liquid products in both the filtrate and the wash solution samples were used as the overall yields of liquid products. The yield of solid product was taken as the weight difference between the solid residue and the catalyst loaded in the reactor. Some of the used catalysts (i.e. recovered solid residue) were further analyzed with TGA (Mettler, TG-50) under a dry air flow from 323 to 1023 K at a heating rate of 5 K/min. An overall mass balance of $> 90\%$ was obtained with this kind of analysis; most experiments show an overall mass balance of $> 95\%$.

3. Results and discussion

3.1. Hydrogenation at 553 K

The results of naphthalene hydrogenation at 553 K over the three noble catalysts studied and the $NiMo/Al_2O_3$ reference catalyst are shown in Table 1. The naphthalene conversions over Pt/Al_2O_3, Pd/Al_2O_3, and Pd/TiO_2 were all above 70% in the 1-h run, compared to a 17% conversion over $NiMo/Al_2O_3$ at a 50% higher catalyst loading. It is clear that the three noble metal catalysts are much more active than the $NiMo/Al_2O_3$ hydrotreating catalyst at this reaction condition. Also included in Table 1 are the hydrogenation results using TiO_2 and HCl treated Al_2O_3 as catalysts; it is obvious that the high activities of these three noble metal catalysts cannot be attributed to the support or the Cl residue in the catalysts. Beside the higher naphthalene conversions with the three noble metal catalysts, the selectivity to hydrogenated naphthalene products (dihydronaphthalene, tetralin, and decalin) and the molar ratios of hydrogen reacted to naphthalene reacted, $\Delta H/\Delta Naph$, are also significantly higher than with the $NiMo/Al_2O_3$ catalyst. The calculated $\Delta H/\Delta Naph$ ratio for the three noble metal catalysts roughly correspond to the amount of hydrogen added to form the hydrogenated products. This indicates that the hydrogen reacted was almost all used for hydrogenation with the noble metal catalysts; whereas for $NiMo/Al_2O_3$ a portion of the hydrogen consumed was used in other reaction routes such as in the formation of gas products. The low yields of solid and gas products over the noble metal catalysts also indicate that the hydrogenolysis of naphthalene was not significant at this reaction condition. It is clear that the noble metal catalysts are more suitable for the low-temperature hydrogenation of naphthalene and, potentially, more suitable for the hydrotreating purposes at 553 K or lower.

It is interesting to note that the main product of the naphthalene hydrogenation is tetralin at

553 K even when the naphthalene conversion is above 90% (Table 1). This trend is similar to that for CoMo/Al_2O_3 catalyst at 623 K [17]. As both naphthalene hydrogenation and tetralin hydrogenation are exothermic reactions, a higher equilibrium yield to more hydrogenated products is expected from thermodynamic considerations when a lower reaction temperature is used. Therefore, naphthalene hydrogenation at 473 K was studied.

3.2. Hydrogenation at 473 K

The results of naphthalene hydrogenation at 473 K are shown in Table 2 for the three noble metal catalysts. It appears that under these conditions tetralin remains essentially the only hydrogenated product, except for those runs with conversion as high as 100%. As decalins would be thermodynamically favorable at this low temperature, it implies that the formation of decalins is kinetically less favorable over the catalysts under the conditions used. However, the hydrogenation abilities of these noble metal catalysts at 473 K are clearly shown from the high selectivity to hydrogenated products, high $\Delta H/\Delta$Naph ratios, as can be seen in Table 2. These results indicate that noble metal catalysts can be useful for low-temperature hydrogenation of polycyclic aromatic compounds.

In Table 2, an increase in the catalyst loading from about 0.13 to approximately 0.2 g (amount

Table 1
Naphthalene hydrogenation over various catalysts at 553 K using tridecane as the solvent

	NiMo/Al_2O_3	Pt/Al_2O_3		Pd/Al_2O_3		Pd/TiO_2		TiO_2	HCl/Al_2O_3
Feed									
Catalyst (mg)	207	127	136	132	137	144	131	132	134
H_2 [a] (psig)	1000	1000	1000	1000	1000	1000	1000	1000	1000
Naph [b] (mg)	1001	1001	1003	1002	1011	1002	1004	1001	1005
Reaction [c]									
Time (h)	1	1	2	1	2	1	2	1	1
ΔH_2 [d] (mmol)	2	10	15	10	16	12	15	3	5
$\Delta H_2/\Delta$Naph [e]	1.5	1.8	2.2	1.7	2.2	1.8	1.9	4	5.8
Yield [f] (mg)	122	804	949	829	992	863	1016	50	72
% Conversion, X_N [g]	17	72	86	77	90	84	98	9	11
Selectivity (wt%) [h]									
di-H-Naph [i]	0.2	0	0	0	0	0	0	0.2	0.3
Tetralin	55	92	85	90	90	92	90	16	6
t-Decalin	0	3	7	2	2	1	6	0	0
c-Decalin	0	2	5	0.7	0.4	0.2	1	0	0
R-(1-ring) [j]	6	0.6	0.6	2	0.5	0.6	0.5	5	3
R-(2-ring) [k]	1	0.1	0.2	0.1	0.1	0.2	0.2	1	0.4
R-(3^+ring) [l]	0	0	0	0	0	0	0	0	2
Solid	0	0.2	0.5	0.3	0.2	0	0	2	2
Gas	38	3	1	5	7	6	3	76	87

[a] 1000 psig = 6.99 MPa. H_2 feed at room temperature to an accuracy of 20 psig.
[b] Naphthalene.
[c] Temperature setting of the sandbath heater is 553 K.
[d] Number of moles of H_2 reacted.
[e] Molar ratio of H_2 reacted to naphthalene reacted.
[f] Overall yield of products listed below.
[g] Naphthalene conversion, calculated from the amount of Naph remained and the amount of Naph fed.
[h] Based on recovered products excluding naphthalene.
[i] Dihydronaphthalene.
[j] R-(1-ring) includes alkylbenzenes and alkylcycloparaffins.
[k] R-(2-ring) includes indenes, indanes, alkyltetralins, alkylnaphthalenes, and biphenyls.
[l] R-(3^+ring) includes species having at least 3-ring structures.

of naphthalene kept constant) significantly increased the naphthalene conversion with any of the three catalysts, Pt/Al_2O_3, Pd/Al_2O_3, and Pd/TiO_2. At 0.2 g catalyst loading, all three noble metal catalysts promoted naphthalene conversion to about 100%. However, their product selectivity patterns are different. The major products with Pd/Al_2O_3 include tetralin, and *cis*- and *trans*-decalin, but only decalins dominate in the products with Pt/Al_2O_3 and Pd/TiO_2. Pt/Al_2O_3 displayed slightly higher selectivity to *cis*-decalin, whereas both Pd catalysts showed higher selectivity to *trans*-decalin. The highest yield to *trans*-decalin was obtained with Pd/TiO_2. These trends are consistent with the results from a collateral study on catalytic hydrogenation in this laboratory [4]. Whether or not the kinetic characteristics of the catalysts also result in this different selectivity to decalins cannot be judged simply from the data shown in Table 2.

The results of naphthalene hydrogenation in the presence of benzothiophene are also included in Table 2. When 9 mg benzothiphene was added (1800 ppm of benzothiphene in the feed), the molar ratios of sulfur to Pt and Pd are 3.3 and 1.8, respectively, and this ratio increases to 7.8 for Pt and 4.3 for Pd catalysts with addition of 21 mg benzothiophene (4200 ppm in the feed). The addition of 1800 ppm benzothiophene caused a 87, 53, and 39% decrease of the naphthalene conversion respectively for the Pt/Al_2O_3, Pd/Al_2O_3, and Pd/TiO_2 catalysts in the 2-h runs; whereas a 90, 84, and 57% decrease was observed respectively when 4200 ppm benzothiophene was added. It is clear that benzothiophene can significantly hinder the hydrogenation activities of noble metal catalysts and a higher sulfur content resulted in a lower conversion during the same period of reaction. However, the above percentage reductions in naphthalene conversion indi-

Table 2
Naphthalene hydrogenation over noble metal catalysts at 473 K using tridecane as the solvent [a]

	Pt/Al_2O_3					Pd/Al_2O_3					Pd/TiO_2					
Feed																
Catalyst (mg)	124	207	191	184	196	135	208	199	195	202	138	214	197	194	191	202
H_2 (psig)	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500	1500
Naph (mg)	1001	1004	1003	1004	1001	1001	1004	1001	1002	1002	1002	1002	1002	1001	1000	1001
BT [b] (mg)	0	0	9	21	21	0	0	9	21	21	0	0	9	21	21	21
Reaction																
Time (h)	2	2	2	2	8	2	2	2	2	8	2	2	2	2	4	8
ΔH_2 (mmol)	4	34	3	2	6	8	29	9	4	10	8	33	7	7	11	17
$\Delta H_2/\Delta$Naph	4.8	4.3	2.9	2.6	7.7	2.5	3.7	2.4	3.2	1.6	2.8	4.2	1.5	2.1	2.3	2.4
Yield (mg)	115	1072	149	120	133	434	1060	500	187	828	388	1068	636	462	656	949
% Conversion X_N	11	100	13	10	10	42	100	47	16	78	37	100	61	43	61	89
Selectivity (wt%)																
di-H-Naph	0	0	0	0	0	0	0	0	0	0	0	0	0.1	0	0	0
Tetralin	44	1	63	20	47	82	36	83	62	93	84	0.5	88	81	89	89
t-Decalin	0	44	0	0	0	0	43	0.5	0	0.3	0.4	76	0.4	0.3	0.2	0.8
c-Decalin	0	49	0	0	0	0	17	0	0	0	0.1	18	0	0.1	0	0.1
R-(1-ring)	3	0	0.2	7	9	1	0	0.8	4	2	2	0	0.8	2	1.9	1.4
R-(2-ring)	2	0	0.1	3	1	0.5	0.1	0.1	2	0.3	0.4	0.1	0.2	0.4	0.4	3
R-(3^+ ring)	0	0	0	0	0	0	0	0	0.4	0	2	0	0.1	0	0	0
di-H-BT [c]	0	0	0	1	0	0	0	0.2	5	0.1	0	0	0	0.8	0.2	0
Solid	6	1	1	11	0	1	0.2	0	0	0.1	0	0	0	0.1	0.1	0.5
Gas	46	6	35	59	43	16	5	15	28	5	12	5	10	15	9	6

[a] See footnotes of Table 1.

[b] Benzothiophene.

[c] Dihydrobenzothiophene.

cate that palladium catalysts are less sensitive to benzothiophene than the platinum catalyst, and that the TiO_2 support is superior over the Al_2O_3 support with respect to the catalytic hydrogenation activity in the presence of benzothiophene. This is generally true when compared either at similar sulfur/catalyst wt ratios or at comparable sulfur/metal molar ratios. For example, the naphthalene conversions over Pd/TiO_2 and Pd/Al_2O_3 catalysts in the presence of a larger amount of sulfur (4200 ppm; S/Pd mol ratio: 4.3) are still higher than that over Pt/Al_2O_3 catalyst with a smaller amount of sulfur (1800 ppm; S/Pt mol ratio: 3.3), and Pd/TiO_2 catalyst is superior to Pd/Al_2O_3 in terms of higher conversion, as can be seen from Table 2. Since the sulfur/metal molar ratio is larger than 1 in all the runs in the presence of benzothiophene, the sulfur added (particularly at the level of 4200 ppm) is enough to cover all the metal surface even with 100% metal dispersion. Therefore, the above results indicate that Pd/TiO_2 and Pd/Al_2O_3 catalysts have higher sulfur tolerance than Pt/Al_2O_3, and in this context the Pd/TiO_2 catalyst is more promising than the other two catalysts.

To see whether the sulfur poisoning of the catalysts is a permanent effect, experiments with an extended reaction period (8 h) were performed. The results in Table 2 show that the naphthalene hydrogenation in the presence of benzothiophene can proceed to a conversion as high as 89 and 78%, respectively, for Pd/TiO_2 and Pd/Al_2O_3. Extending the reaction time with the Pd catalysts from 2 to 8 h resulted in gradual recovery of naphthalene conversion. This indicates that hydrogenation activity of the Pd catalysts can be recovered as a result of concomitant hydrodesulfurization. However, the sulfur poisoning on Pt/Al_2O_3 catalyst seems to be permanent as no recovery was observed by extending the reaction time. The reason why Pd catalysts showed better sulfur tolerance than the Pt catalyst is not clear at present. Not only the type of the metal and support but also the pretreatment condition employed can cause a difference. Arcoya et al. [18] proposed that as the electron-donating character of palladium atoms decreases the metal becomes more sulfur-tolerant. Since the Pd/Al_2O_3 catalyst used in this study was pretreated in 20% O_2, positively charged Pd which could exist in this catalyst. However, this would not apply to Pd/TiO_2 catalyst since the hydrogen pretreatment at 473 K was found to be sufficient to reduce Pd to its zero-valence state. On the other hand, Chen et al. [9] found that Pt/TiO_2 showed higher resistance to H_2S than Pt/Al_2O_3 and suggested that the labile oxygen in TiO_2 could react with H_2S to form SO_x. This provides an insight to how the support may affect the sulfur-resistance of noble metal catalysts, and this effect may account for why extending the reaction time restored the catalyst activity in the presence of H_2S generated from benzothiophene conversion (see below). However, it is difficult to identify what the so-called labile oxygen is and how it could be generated [9]. TiO_2 supported noble metal catalysts have been known to have metal-support interaction where the TiO_2 is partially reduced. The factors that could change the sulfur resistance of the Pd/TiO_2 catalyst include partial reduction of TiO_2, a special active site at the interfacial region, electronic interactions between metal and support, and even formation of palladium hydride. Further study on the origin of sulfur tolerance is needed.

It should be noted that no benzothiophene was identified in the liquid products from all the runs with the addition of benzothiophene. In the runs with Pt/Al_2O_3, it is likely that benzothiophene was adsorbed strongly on the surface rendering deactivation. The situation is different with Pd/TiO_2 and Pd/Al_2O_3. That the hydrogenation reaction approached completion with extended reaction time indicates that benzothiophene was gradually converted (on Pd/TiO_2 and Pd/Al_2O_3) to other sulfur species which do not deactivate the catalyst seriously as compared to benzothiophene. It is worthy noting the yield (selectivity times conversion) of ethylbenzene included in the R-(1-ring) category in Table 2, which increased with reaction time in the runs with added benzothiophene. The yield of ethylbenzene with Pd/TiO_2 were 55.6, 75.3, and 79.9 mol% based on benzothiophene at 2, 4, and 8 h, respectively. Moreover, the partial hydrogenation product of benzothiophene, dihydrobenzothiophene, was detected in the products. The yield of dihydrobenzothiophene with Pd/TiO_2 were 17.4, 6.2 and 0 mol% based on benzothiophene at 2, 4, and 8 h, respectively. On the basis of these results, it is likely that the conversion of the benzothiophene over the Pd catalysts proceeded via a hydrodesulfurization reaction to form ethylbenzene and hydrogen sulfide with dihydrobenzothiophene as the intermediate. Accordingly, the hydrogen sulfide formed does not deactivate the palladium catalysts as much as benzothiophene does.

Fig. 1 shows the selectivities to tetralin and decalins as a function of naphthalene conversion. Though the presence of benzothiophene in the feed decreased naphthalene conversion, it is interesting to note that the selectivity to hydrogenated naphthalene products were not significantly affected. It can be observed from Fig. 1 that tetralin is the dominant product except in the region where naphthalene conversion approaches 100%, regardless of the presence of benzothiophene. This trend in product selectivity coincides with that presented in Table 1 for naphthalene hydrogenation at 553 K and that reported for CoMo/Al_2O_3 at 623 K [17]. This indicates that the effect of benzothiophene is likely site-blocking rather than electronic interaction, and that naphthalene hydrogenation could occur concurrently with the benzothiophene hydrodesulfurization. These results suggest that some noble metal catalysts can be useful for low-temperature hydrotreating purpose even when the feed contains sulfur.

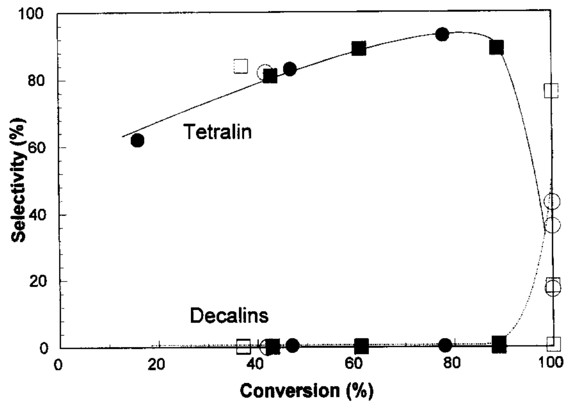

Fig. 1. Selectivity to tetralin and decalins as a function of naphthalene conversion during the naphthalene hydrogenation at 473 K over Pd/Al_2O_3 (○, ●) and Pd/TiO_2 (□, ■). Open symbols: runs without benzothiophene; filled symbols: runs in the presence of benzothiophene.

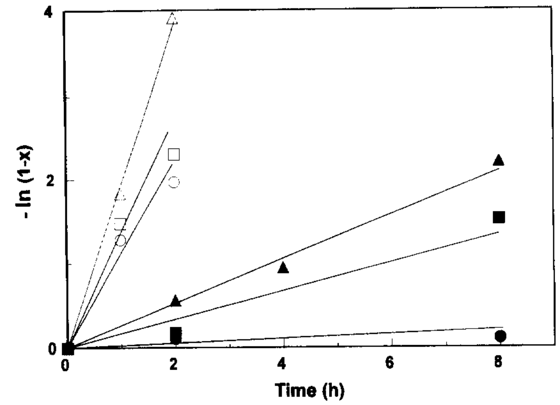

Fig. 2. Pseudo-first-order plot of the naphthalene hydrogenation over Pt/Al_2O_3 (○, ●), Pd/Al_2O_3 (□, ■) and Pd/TiO_2 (△, ▲). Open symbols: runs at 553 K without benzothiophene; filled symbols: runs at 473 K in the presence of benzothiophene.

3.3. *Quantitative estimation of sulfur resistance*

In an effort to obtain a quantitative analysis of the effect of benzothiophene on the naphthalene hydrogenation over these noble metal catalysts, we performed a pseudo-first order kinetic analysis. The apparent rate constants can be estimated by the slopes, as in Fig. 2, where the results reported for the naphthalene hydrogenation at 553 K (Table 1) and the hydrogenation at 473 K in the presence of 4200 ppm sulfur (Table 2) are presented accordingly. The effect of benzothiophene on the rate of naphthalene hydrogenation is then estimated by the ratio of the apparent rate constant in the presence of benzothiophene to that without benzothiophene, i.e. k_s/k. After correction for the amounts of catalysts used in different runs, the k_s(473 K)/k(553 K) ratio was found to be 0.1, 0.12, and 0.02 for Pd/TiO_2, Pd/Al_2O_3, and Pt/Al_2O_3, respectively. If the activation energy that Nieuwstad et al. [7] reported for 2-methylnaphthalene hydrogenation over Pd/C catalyst, 10 kcal/mol, is used to correct for the effect of reaction temperature, then the k_s(473 K)/k(473 K) ratio becomes 0.46, 0.56, and 0.1 respectively for Pd/TiO_2, Pd/Al_2O_3, and Pt/Al_2O_3. This again indicates that the palladium catalysts are less affected by the presence of benzothiophene. Based on the equation reported by Lo [5,19] and the benzothiophene concentration used in this study, a k_s/k ratio of 0.73 was estimated for NiMo/Al_2O_3 at 623 K; the k_s/k ratios of the two palladium catalysts at 473 K are practically comparable. This indicates that the palladium catalysts are comparable to NiMo/Al_2O_3 for simultaneous hydrogenation and hydrodesulfurization even at a lower reaction temperature when NiMo/Al_2O_3 catalyst shows little activity.

3.4. TGA analysis

The results of TGA analysis of the fresh and used Pd/Al_2O_3 catalysts are shown in Fig. 3. For the sample that was exposed to the reaction mixture at room temperature for 30 min (b), two broad weak weight loss features appear at approximately 443 and 693 K. The former feature cannot be unambiguously explained since it is within the region where moisture desorbs, while the latter is considered as the naphthalene adsorbed on the catalyst since no reaction would occur at this condition. This 693 K weight loss feature can also be observed for other Pd/Al_2O_3 samples whose reaction conversion were less than completion. For the sample tested at 473 K for 2 h (d), the 693 K feature cannot be identified, likely due to the fact that the conversion level was as high as 100%. For the sample used for the reaction in the presence of benzothiophene (e), this 693 K feature is only barely above the noise level of the baseline which implies that the surface coverage of naphthalene was low when the benzothiophene present. This is consistent with the discussion above that benzothiophene may be preferentially adsorbed. The new feature appearing at around 473 K with the sample tested with benzothiophene could be due to the adsorbed benzothiophene, but it needs further experiments to verify this.

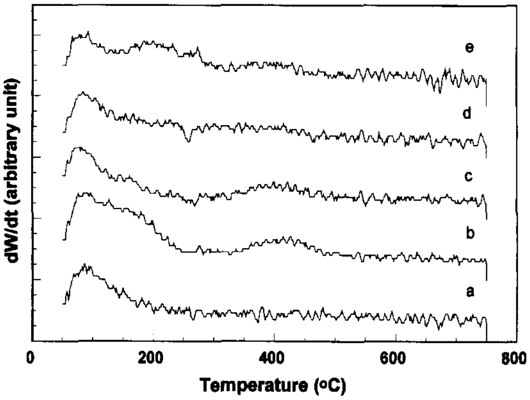

Fig. 3. TGA results of fresh and used Pd/Al_2O_3 catalysts: (a) fresh, (b) exposed to reaction mixture at room temperature for 30 min, (c) reaction at 553 K for 2 h, (d) reaction at 473 K for 2 h, and (e) reaction at 473 K for 2 h in the presence of benzothiophene.

Comparison between Pd/TiO_2 and Pt/Al_2O_3 samples tested with or without benzothiophene is given in Fig. 4. For the two used Pt/Al_2O_3 samples, only in the region below 473 K can

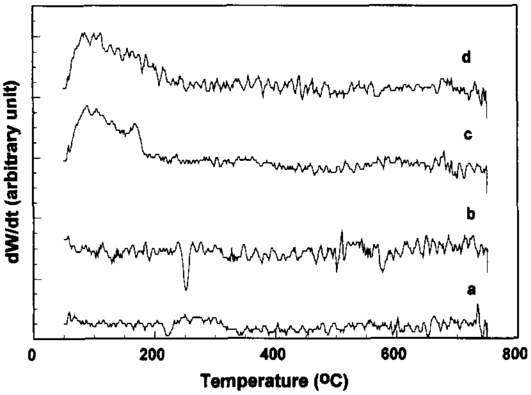

Fig. 4. TGA results of used catalysts after reaction at 473 K for 2 h: (a) Pd/TiO_2 with no addition of benzothiophene, (b) Pd/TiO_2 in the presence of benzothiophene, (c) Pt/Al_2O_3 without benzothiophene, and (d) Pt/Al_2O_3 in the presence of benzothiophene.

TGA features be observed which make unambiguous attribution impossible owing to the possible interference from the moisture. Pd/TiO_2 (a) was found to contain very little moisture feature and a small weight gain feature around 493 K which shifts to higher temperature when benzothiophene is present in the feed (b). An oxidation of either the reduced Pd or the partially reduced TiO_2 could cause this feature. The oxidation of reduced Pd is considered less likely because it was not observed in Pd/Al_2O_3 samples and because all the samples used in TGA analysis had been air-exposed. Although no report on the partial reduction of TiO_2 after a 473 K H_2 pretreatment was found in the literature, an O_2 adsorption isobar of TiO_2 indicated that O_2 adsorption at around 473 K is possible for activated TiO_2 [20]. Therefore, the weight gain feature of Pd/TiO_2 might be due to the interaction between O_2 and activated TiO_2, e.g. partially reduced TiO_2 either due to the pretreatment or due to the reducing environment of the reaction. If this speculation is true, its shift to higher temperature when tested in the presence of benzothiophene indicates that benzothiophene might interact with the partially reduced TiO_2. Finally, TGA results showed that there is no coking problem with these noble metal catalysts under the reaction conditions used. This is another potential advantage of low-temperature catalytic hydrogenation with the noble metal catalysts.

3.5. Thermodynamic and kinetic considerations

The equilibrium of the naphthalene hydrogenation and its reverse reaction has been studied by Frye [21] and by Frye and Weitkamp [22]. The equilibrium constants were found to be well below 0.1 for naphthalene hydrogenation to either tetralin or decalins at a temperature of 573 K or above, indicating that the reaction is thermodynamically unfavorable at higher reaction temperatures. Similarly, the hydrogenation of phenanthrene and other polycyclic aromatic compounds was also found to be thermodynamically unfavorable at higher temperature [5,21]. However, the industrial hydrotreating process for improving hydrogen/carbon ratio of heavy liquids typically uses a temperature above 623 K and a high hydrogen pressure with catalysts such as NiMo/Al_2O_3. The heavy liquids, especially those from coal liquefaction, contain a significant amount of aromatics and polycyclic aromatic compounds. Thus, a high hydrogen pressure is necessary if high conversion is desired.

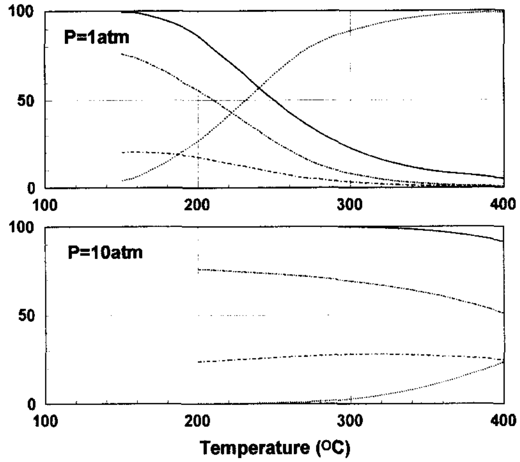

Fig. 5. Calculated equilibrium conversion (%) of naphthalene and product selectivity (%) as a function of reaction temperature (see text for details). Conversion of naphthalene (—), selectivity to tetralin (· · ·), selectivity to *trans*-decalin (- - -), and selectivity to *cis*-decalin (-· · -).

Fig. 5 shows the trends of equilibrium conversions of naphthalene and the selectivity of its hydrogenated products as a function of reaction temperature, which were derived by calculations based on the equilibrium constants reported by Frye and Weitkamp [22]; a feed with the hydrogen/naphthalene ratio of 13, and a total pressure of either 1 or 10 atmosphere; the assumption of ideal gas mixture was imposed for simplification. It is clear that the equilibrium conversion decreases with increasing temperature and that tetralin becomes the dominate product at higher temperatures where the naphthalene conversion drops below ca. 80%. A high reaction pressure obviously shifts these trends to higher temperature range. Fig. 5 also shows that the reaction at lower temperature and a lower pressure could have the same thermodynamic equilibrium as the reaction at higher temperature and higher pressure. Thus, a lower temperature hydrotreating process is thermodynamically feasible beside having higher energy efficiency.

In addition to the thermodynamics, the kinetic aspects would also determine whether a lower-temperature hydrotreating process is technically feasible. The conventional hydrotreating catalysts operating at the temperature above 623 K usually have the advantage of being inexpensive and capable of simultaneous hydrodesulfurization, hydrodenitrogenation, and hydrodeoxygenation. However, these catalysts are relatively inactive at a temperature below 573 K; therefore, other types of catalysts should be examined when a lower-temperature hydrotreating process is desired. Supported group VIII catalysts have been used for hydrogenation reactions over a wide temperature range, and have shown significant activities for the hydrogenation of aromatic compounds at temperatures below 473 K [1,6,7]; therefore, they could be the candidates for low-temperature hydrotreating catalysts. Although the noble metal catalysts were found easily poisoned by sulfur [8], recent studies showed that sulfur resistance of Pt and Pd catalysts are affected by factors such as the valence state of metal [18,23], the type of support [9,11,23,24], the preparation procedure [10], the extent of presulfidation [25], etc. This implies that tailoring the supported noble metal catalysts may improve the sulfur resistance and make useful catalysts for low-temperature hydrotreating purpose.

From Tables 1 and 2, the three noble metal catalysts studied showed their potentials for applications in the polycyclic aromatic hydrogenation and hydrotreating purposes. The high activities of group VIII metal catalysts (Pt, Pd, Ni) toward hydrogenation of alkylbenzenes and of polycyclic aromatic compounds have been known for some time; their activities toward hydrogenation of polycyclic aromatic compounds can be orders of magnitude higher than the conventional hydrotreating catalysts such as NiMo/Al_2O_3 [1]. Even the presulfided Pt and Pd catalysts showed significantly higher hydrogenation activities and C–N hydrogenolysis activities than sulfided Mo catalyst [26]; this indicates that sulfur-poisoned noble metal catalysts might still have comparable activities to the conventional hydrotreating catalysts. Thus, in terms of higher energy efficiency and higher activity of the catalyst, the use of some noble metal catalysts for low-temperature hydrotreating purposes could become an attractive option in the future. However, more detailed studies are needed before effective implementation of supported noble metal catalysts for these applications.

4. Summary

The present study, though still preliminary, has shown that noble metal catalysts such as Pt and Pd supported on Al_2O_3 and TiO_2 can be used for low-temperature hydrogenation of polyaromatic hydrocarbons, and they display catalytic activity even in the presence of sulfur in the feed ranging from 1800 to 4200 ppm. The Pd catalyst shows high sulfur resistance than Pt when supported on Al_2O_3, and the sulfur tolerance is even higher when Pd is loaded onto TiO_2 support. The potential of Pd/TiO_2 as a sulfur-tolerant catalyst for low-temperature hydrotreating warrants further detailed study.

5. List of symbols

$(MW)_{air}$	average molecular weight of air
$(MW)_g$	average molecular weight of the gas products (excluding hydrogen)
$(MW)_{H_2}$	molecular weight of hydrogen
$(MW)_{vent}$	average molecular weight of the vent gas after reaction;

$(n_{H_2})_{feed}$	number of moles of hydrogen loaded initially
$(n_{H_2})_{vent}$	number of moles of hydrogen in the vent gas
P_{atm}	atmospheric pressure
P_{Rxn}	pressure of the tubing bomb after reaction at room temperature, read from the gauge atop the tubing bomb
R	gas constant
T_r	room temperature;
V_{lf}	liquid volume in the tubing bomb, estimated by the solid and liquid feed
V_{lp}	liquid volume in the tubing bomb after the reaction, estimated by the solid and liquid unloaded
V_{Rx}	total inner volume of the tubing bomb;
$(wt)_{air}$	weight of air inside the tubing bomb before loading hydrogen
$(\Delta wt)_{H_2}$	weight difference before and after loading hydrogen prior to reaction, measured by a laboratory balance
$(\Delta wt)_{vent}$	weight difference before and after venting the tubing bomb after reaction, measured by a laboratory balance
y_{H_2}	mole fraction of hydrogen in the vent gas

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Appendix A. Gas yield and hydrogen consumption calculations

The estimations of hydrogen consumption and total gas yields are important in understanding the extent of hydrogenation reaction and the effect of hydrotreating, as well as in evaluating the catalyst performance. A simple approach is described below which is based only on the weight changes of the tubing bomb during its loading and unloading and the average molecular weight of gas products (excluding hydrogen) identified from gas chromatography. This approach uses two assumptions: (i) the ideal gas law is valid at room temperature and the pressure of reaction loading, and (ii) the gas solubility in the solvent inside the bombs at room temperature and the loading pressure can be neglected. These may seem oversimplified but in considering the experimental uncertainties it provides reasonable estimations of the hydrogen consumption and the gas yield. That the calculated $\Delta H/\Delta$Naph ratios in Tables 1 and 2 show agreement with the product distribution obtained from the chromatography validates this approach.

A.1. Procedures

1. Calculate the amount of hydrogen loaded in the tubing bomb before initiating the reaction:

$$(n_{H_2})_{feed} = \frac{[(\Delta wt)_{H_2} + (wt)_{air}]}{(MW)_{H_2}}$$

or alternatively,

$$(n_{H_2})_{feed} = \frac{P_{feed}(V_{Rx} - V_{lf})}{RT_r}$$

2. Calculate the average molecular weight of the vent gas after the reaction is quenched to room temperature:

$$(\Delta wt)_{\mathrm{vent}} = \frac{P_{\mathrm{Rxn}}(V_{\mathrm{Rx}} - V_{\mathrm{lp}})(MW)_{\mathrm{vent}}}{RT_{\mathrm{r}}} - \frac{P_{\mathrm{atm}}(V_{\mathrm{Rx}} - V_{\mathrm{lp}})(MW)_{\mathrm{vent}}}{RT_{\mathrm{r}}}$$

$$\therefore (MW)_{\mathrm{vent}} = \frac{(\Delta wt)_{\mathrm{vent}} RT_{\mathrm{r}}}{(V_{\mathrm{Rx}} - V_{\mathrm{lp}})(P_{\mathrm{Rxn}} - P_{\mathrm{atm}})}$$

3. Calculate the average molecular weight of the vent gas based on the gas chromatography analysis on the collected gas sample, in which hydrogen is excluded:

$$(MW)_{\mathrm{g}} = \frac{\text{Total weight}}{\text{Total number of moles}} = \frac{\sum (\text{Peak area}/\text{Response factor of weight})_{\mathrm{i}}}{\sum (\text{Peak area}/\text{Response factor of mole})_{\mathrm{i}}}$$

4. Calculate the mole fraction of hydrogen in the vent gas:

$$(MW)_{\mathrm{vent}} = (MW)_{\mathrm{g}}(1 - y_{\mathrm{H_2}}) + (MW)_{\mathrm{H_2}} y_{\mathrm{H_2}}$$

$$\therefore y_{\mathrm{H_2}} = \frac{(MW)_{\mathrm{g}} - (MW)_{\mathrm{vent}}}{(MW)_{\mathrm{g}} - (MW)_{\mathrm{H_2}}}$$

5. Calculate the hydrogen consumption on molar basis:

$$(n_{\mathrm{H_2}})_{\mathrm{vent}} = \frac{P_{\mathrm{Rxn}}(V_{\mathrm{Rx}} - V_{\mathrm{lp}}) y_{\mathrm{H_2}}}{RT_{\mathrm{r}}}$$

$$\therefore \mathrm{H_2}\ \text{consumption} = (n_{\mathrm{H_2}})_{\mathrm{feed}} - (n_{\mathrm{H_2}})_{\mathrm{vent}}$$

6. Calculate the gas yield in weight basis:

$$\text{Gas yield} = \frac{P_{\mathrm{Rxn}}(V_{\mathrm{Rx}} - V_{\mathrm{lp}})(1 - y_{\mathrm{H_2}})(MW)_{\mathrm{g}}}{RT_{\mathrm{r}}}$$

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