

The thioresistance of platinum/aluminum borate catalysts in aromatic hydrogenation

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Abstract

Naphthalene and benzothiophene dissolved in n-hexadecane were used as model compounds to simulate the aromatics and sulfur compounds in diesel fuels for hydrogenation activity and sulfur tolerance tests. The aluminum borate (AB_x) supports were prepared with coprecipitation method. Pt/aluminum borate (Pt/AB) catalyst had a higher thioresistance than Pt/ γ -Al₂O₃ catalyst due to the higher acidity of AB_x support than γ -Al₂O₃ support. When the aluminum boron atomic ratio (Al/B) increased, the acidity of AB support increased, and the thioresistance of Pt/AB catalyst increased, too. The catalysts Pd/AB_x had higher hydrogenation activity and sulfur resistance than Pd/ γ -Al₂O₃, but lower than Pt/AB_x catalysts. When boron was added to the Pt/ γ -Al₂O₃ catalyst, it improved the sulfur tolerance of catalyst due to increasing the acidity of supports. Experimental results indicated that more sulfur compound could be adsorbed at lower temperature and higher sulfur concentration, although parts of the sulfur compounds were reversible adsorbed.

Keywords: Aluminum borate; Hydrogenation; Naphthalene; Thioresistance; Platinum

1. Introduction

High aromatics content in diesel fuel lowers fuel quality and contributes significantly to the formation of undesired emissions in exhaust gases [1–3]. The environmental regulations governing the composition of diesel fuels and the limitations of aromatics will be tightened in the future. Due to stringent environmental regulations with regard to aromatics content in diesel fuel, aromatics reduction has become a key upgrading parameter in processing middle distillates [4,5].

For the conventional hydrotreating catalysts to achieve acceptable aromatic reduction, severe operation conditions such as high temperatures,

low space velocities and high pressures were found to be necessary. Noble-metal catalysts are known to be deactivated rapidly due to the adsorption of sulfur-containing compounds which are present in industrial feedstocks [6]. A severe pretreatment is necessary to reduce the sulfur content to a level that does not affect the performance of the noble metal catalysts [7].

In recent years, a considerable attention has been paid to develop new catalysts and processes for aromatics saturation in diesel fuel. The most famous process is conventional hydrotreating catalysts (sulfided CoMo/ γ -Al₂O₃, NiMo/ γ -Al₂O₃ and NiW/ γ -Al₂O₃) in first-stage operation and noble metal catalysts in second-stage operation [8]. Extensive research has been done to develop sulfur-tolerant noble metal catalysts by various

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catalyst manufacturing companies such as Shell, Criterion, Amoco and Topsoe. Noble metal (e.g., Pt or Pd) on supported zeolite catalysts has been receiving more attention in recent years as an aromatics hydrogenation catalyst [8–10].

Generally, hydrogenation noble metal catalysts have been supported on γ - Al_2O_3 , activated carbon, SiO_2 and SiO_2 - Al_2O_3 [11–14]. Aluminum borate has been found to be a good catalyst and a good support material for various reactions. Pine [15] employed alumina–boria compound in the hydrocarbon conversion process. Tanabe [16] has shown that alumina–boria catalysts can be used as cracking catalysts. Tsai et al. [17] have shown that aluminum borate is a good support for hydrodesulfurization catalysts. Chen and Li [18] and Li et al. [19] found that the Pt/aluminum borate catalyst had high activity for hydrogenation of cyclohexene and nitrobenzene at atmosphere. Our works [20] have shown that the Pt/Aluminum borate catalysts have good aromatics hydrogenation activity in diesel fuels.

The extent of sulfur-poisoning may vary for different reactions, and it depends upon (1) the organic compounds undergoing reaction, (2) the kinds of sulfur compounds, (3) the conditions of reaction, and (4) the properties of catalyst [21].

In this study, the incipient-wetness impregnation method and co-precipitation method were used to prepare two series of aluminum borates with different Al/B atomic ratio. Naphthalene dissolved in n-hexadecane was used as a model compound to simulate the aromatics in diesel fuels. Benzothiophene was dissolved in this solution to simulate the sulfur compounds in diesel fuel. Hydrogenation activity of naphthalene (bi-aromatic) and thioresistance over Pt(Pd)/aluminum borate catalysts were studied with a trickle bed reactor at high pressure (5.17 MPa). The chemical and physical properties of these catalysts were characterized in order to correlate with their catalytic and sulfur tolerant properties. The effects of reaction conditions on the thioresistance of catalysts were also studied.

2. Experimental

2.1. Preparation of aluminum borate support

The aluminum borate supports were prepared by the impregnation and coprecipitation methods. The impregnated catalyst was obtained by impregnating γ -alumina (Cs-331-4, United Catalysts Inc.) with aqueous boric acid (Merck) followed by drying in air overnight and at 383 K for 4 h, and then calcination at 773 K for 6 h. The aluminum boron atomic ratios, (Al/B), of the supports were varied by the amount of impregnated boric acid. For convenience, these supports were denoted as B_x - Al_2O_3 , where x represented the Al/B atomic ratio.

The coprecipitated supports were prepared by neutralizing the mixed solution of aluminum nitrate and boric acid with ammonium hydroxide solution. The detailed preparation procedures were described in our previous paper [20]. The size of these homemade supports was 1.6 mm of diameter, and 3–5 mm of length. For convenience, these supports were denoted as AB_x , where x represented the Al/B atomic ratio.

2.2. Preparation of aluminum borate/aluminum phosphate (ABAP) supports

The ABAP supports were prepared by the same method as AB_x supports, except the mixed acid solution including aluminum nitrate, boric acid, and phosphoric acid. For convenience, these supports were denoted as AB_xAP_y , where x represented the Al/B atomic ratio and y represented Al/P atomic ratio.

2.3. Preparation and characterization of catalyst

The supports employed to prepare catalysts including homemade AB_x , B_x - Al_2O_3 , AB_xAP_y , and commercial γ -alumina Cs-331-4 (United Catalysts Inc.). For the preparation of Pt-catalyst, the supports were impregnated with appropriate amounts of aqueous solution of chloroplatinic acid

(H_2PtCl_6 , Merck products). These catalysts were denoted as Pt/support. When the supports were impregnated with diammineplatinum(II) nitrile [$\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$] solution (Strem Chemicals products), the prepared catalysts were denoted as Pt*/support. For the preparation of Pd-catalyst, the supports were impregnated with appropriate amounts of aqueous solution of palladium chloride (Merck products, dissolved in HCl) [22]. Impregnated supports were kept in air overnight and calcined at 383 K for 4 h, followed by 673 K for 4 h. The noble metal content of the Pt-catalysts was 0.6 wt% and the noble metal content of Pd-catalysts was 1.0 wt%.

The surface area (BET) and pore volume of the support and catalyst were determined from the nitrogen adsorption–desorption isotherms at 77 K, using Micromeritics 2400 apparatus. The measurements were performed on the oxidized form of the catalyst samples.

Catalysts were characterized in terms of exposed metallic surface area and metal dispersion by selective chemisorption with carbon monoxide. Carbon monoxide uptake was determined in a constant volume, high vacuum apparatus with Micromeritics Chemisorb 2800. The stoichiometric ratio of CO to platinum surface atom was supposed to be 1:1 [23]. The volume of CO adsorbed for monolayer coverage was obtained by the difference between total adsorption and physical adsorption [24].

The actual Pt content of Pt/ Al_2O_3 was 0.63 wt%, and the actual Pd content of Pd/ Al_2O_3 was 0.98 wt%. These values were determined by inductively coupled plasma–atomic emission spectrometer (Jarrell–Ash, model 1100).

The Pt metal profile along the pellet diameter was determined by electron probe microanalyzer (JEOL JSMr840 multi-function SEM) with wavelength dispersion spectrometer.

2.4. Reactants used

The model compound, naphthalene (Merck products, purity > 99%) was used to determine the hydrogenation activity of catalysts. The sol-

Table 1
The physical properties of compounds employed and reaction products

Compound	m.p. (K)	b.p. (K)
naphthalene	353.5	490.0
tetralin	242.0	480.0
<i>trans</i> -decalin	242.6	460.2
<i>cis</i> -decalin	229.7	468.7
benzothiophene	305.0	494.1
n-hexadecane	291.0	553.0

vent used in this work was n-hexadecane (Merck Products, purity > 99%). High purity of hydrogen (purity > 99.99%) was used in the reaction system. The sulfur compound, benzothiophene (Aldrich Chemical Products, purity > 99%), was added to the feed to test the sulfur-tolerance of the catalysts. The physical properties of employed compounds and reaction products are listed in Table 1.

2.5. Reaction system

The bench-scale reaction system with concurrent downflow trickle bed reactor was used in this study, as shown in our previous paper [20]. The reactor was heated and controlled by three electric resistances and three temperature controlled (Eurotherm Co.). The hydrogen gas flow rate was measured and controlled by Brooks mass flowmeter and controller. Liquid feed, 10 wt% naphthalene dissolved in n-hexadecane, was supplied by a Gasukuro Kogyo HPLC pump. When the sulfur-tolerance of catalyst was tested, the sulfur-containing compounds were added to liquid feed by another HPLC pump and the total liquid feeds contained 10 wt% naphthalene, 242 ppm S and about 90 wt% n-hexadecane.

The catalyst bed was diluted with ceramics powder (45–80 mesh) to avoid dispersion effect and to obtain a homogeneous thermal distribution in the reactor [17,25]. The remaining spaces of catalyst bed at the top and the bottom of reactor were filled with ceramics powder to avoid the entrance and exit effects.

Catalysts were reduced in situ by H_2 at 673 K for 4 h. The reactor was cooled to the desired temperature before the reactants were introduced. At an appropriate time, the liquid samples were withdrawn from the separator with a sampling valve and analyzed by gas chromatograph (Carlo Erba, Model 6000), equipped with a flame ionization detector (FID) and an electronic integrator (Carlo Erba, Model DP 700). A 10 m by 0.53 mm fused-silica wide-bore column, type WCOT, with liquid phase CP-SIL-5CB, was used to separate reactants and products. The chromatographic analysis was conducted under temperature programming conditions.

3. Results and discussion

3.1. Catalyst characterization

The BET surface areas, pore volumes, pore sizes, and metal dispersion of Pt/Bx- Al_2O_3 , Pt/ Al_2O_3 , Pt*/ Al_2O_3 and Pd/ Al_2O_3 catalysts are compared and listed in Table 2. The results show

that the surface area, pore volume and pore size of the Cs-331-4(γ - Al_2O_3) support was not changed by impregnation of H_2PtCl_6 , $PdCl_2$ or $Pt(NO_2)_2(NH_3)_2$. However, the surface area of Pt/Bx- Al_2O_3 catalyst was decreased, and its pore size was increased when too much borate was impregnated into catalyst. This is possibly due to the plugging of small pores of alumina by impregnation of borate [20]. These results are in agreement with those reports in the literature [26,27].

According to the result of J.M. Basset et al. [28], Pt-catalyst obtained by impregnation with the complex $Pt(NO_2)_2(NH_3)_2$ had the large Pt metal particle, i.e. low Pt metal dispersion. Their result agrees with our result that the metal dispersion of catalyst Pt*/ γ - Al_2O_3 is lower than Pt/ γ - Al_2O_3 , as shown in Table 2.

The BET surface areas, pore volumes, pore sizes, and metal dispersions of Pt/ABx catalysts with different Al/B ratios and Pt/ABxAPy catalysts are listed in Table 3. The pore size distributions of Pt/ABx catalysts show the lack of any bimodal pore size distribution, as can be seen from Fig. 1. These results are in agreement with those

Table 2
The characteristics of different catalysts

Support/catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore radius (nm)	Metal Pt dispersion
1. Fresh support	198.9	0.658	6.58	
2. Prepared catalyst				
Pt/ γ - Al_2O_3	195.0	0.668	6.62	0.924
Pt*/ γ - Al_2O_3	192.7	0.650	6.75	0.719
Pd/ γ - Al_2O_3	192.9	0.660	6.84	—
Pt/B32- Al_2O_3	189.4	0.656	6.79	0.897
Pt/B16- Al_2O_3	192.2	0.716	6.46	0.832

Table 3
The characteristics of Pt/ABx and Pt/ABxAPy catalysts

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore radius (nm)	Metal dispersion CO/Pt
Pt/AB1	257.0	0.404	2.30	0.626
Pt/AB2	325.0	0.422	2.40	0.839
Pt/AB3.5	278.4	0.443	2.91	0.831
Pt/AB5	338.6	0.529	2.76	0.887
Pt/AB8	305.7	0.454	2.20	0.798
Pt/AB16	272.3	0.429	2.30	0.718
Pt/AB5AP10	178.0	0.678	6.44	—
Pt/AB16AP16	198.9	0.576	5.12	—

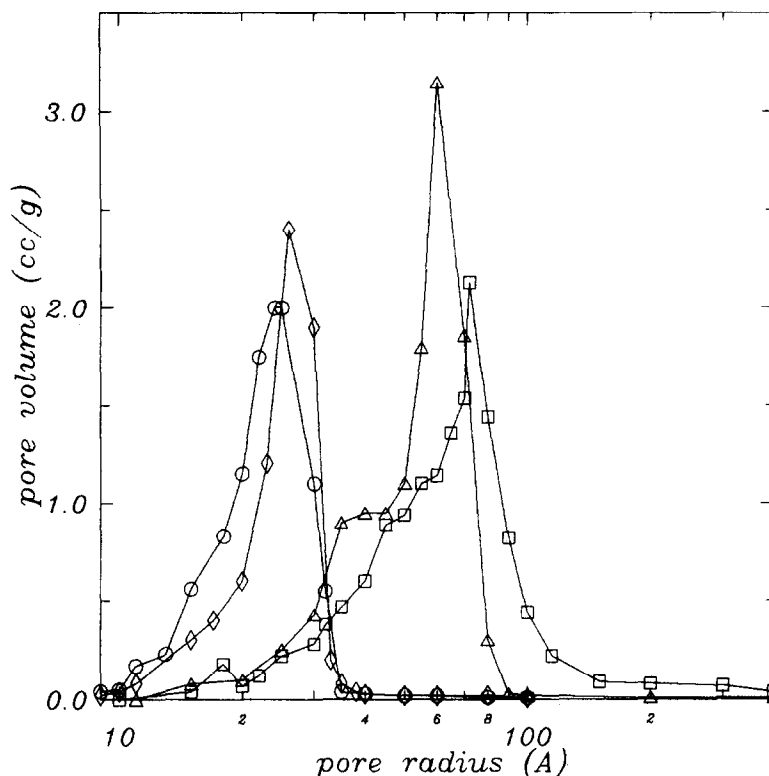


Fig. 1. Pore size distribution of different catalysts. \circ Pt/AB5, \square Pt/AB5AP10, \triangle Pt/Cs-3331-4, \diamond Pt/AB3.5.

in the literature [17,26,29]. The metal dispersions of Pt/ABx catalysts are good, except that of Pt/AB1 catalyst. However, the metal dispersion of Pt/ABx catalyst is not so good as Pt/Al₂O₃ catalyst.

The pore size distributions of Pt/AB3.5, Pt/AB, Pt/Cs-331-4 and Pt/AB5AP10 are shown in Fig. 1. The pore sizes of Pt/ABx catalysts are the smallest of the three catalysts. In general, the pore size of ABx supports is small. The phosphorus was added into ABx for the preparation of ABxAPy support in order to increase the pore sizes of supports and the particle diffusion coefficients of catalysts. The pore size of prepared ABxAPy support is larger than ABx supports, as shown in Fig. 2 and Table 3.

The Pt metal distributions of Pt/Al₂O₃, Pt*/Al₂O₃, Pt/B16–Al₂O₃ and Pt/AB3.5 catalysts are shown in Fig. 2 and Fig. 3. The catalysts Pt/B16–Al₂O₃ and Pt*/Al₂O₃ have uniform Pt metal distribution in catalysts. It is still unknown why adding boron to Pt/Al₂O₃ makes the Pt metal more

uniform distribution in pellet. It is obvious that impregnation with chloroplatinic acid solution leads to a distribution in which the platinum is highly concentrated toward the outer regions of

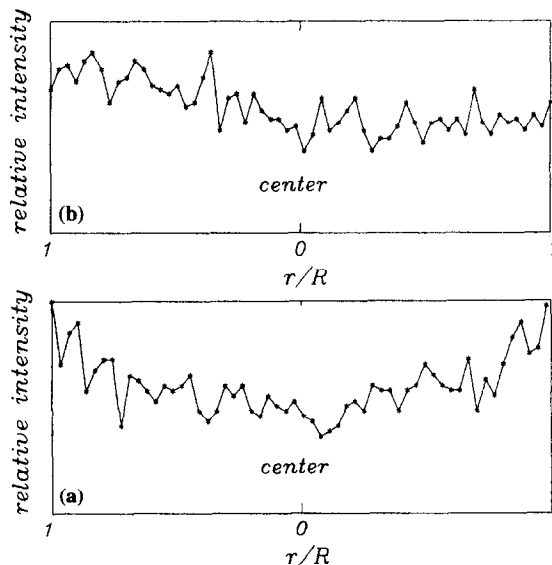


Fig. 2. The Pt metal profiles of the Pt/Al₂O₃ catalysts. (a) Pt*/Cs-3331-4, (b) Pt*/Cs-331-4.

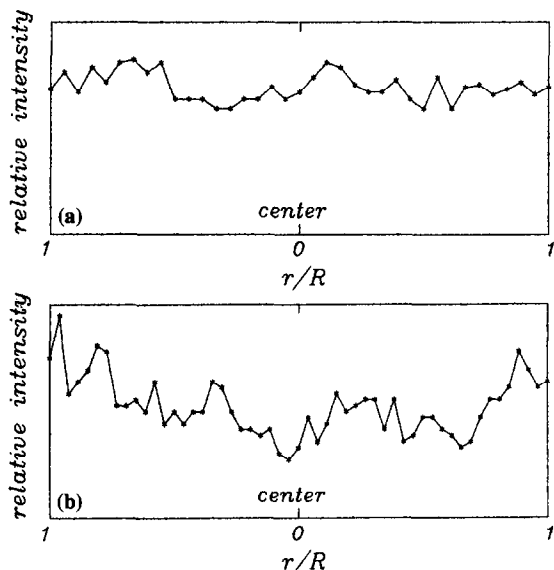


Fig. 3. The Pt metal profiles of the Pt/aluminum borate catalysts. (a) Pt/B16–Al₂O₃, (b) Pt/AB3.5.

the support due to strong chloroplatinic acid adsorption on the support. However, the impregnation with Pt(NO₂)₂(NH₃)₂ solution leads to a nearly uniform platinum distribution [30] because Pt(NO₂)₂(NH₃)₂ is not adsorbed presumably on support, as shown in Fig. 2. The catalyst Pt/AB3.5 is the least uniform Pt distribution which may be due to too small pore size of support AB3.5 to diffuse HPtCl₆⁻ into the internal part of support, and absorbing HPtCl₆⁻ strongly at the periphery because of the high acidity of support.

3.2. The thioresistance of Pt/Bx–Al₂O₃ catalysts

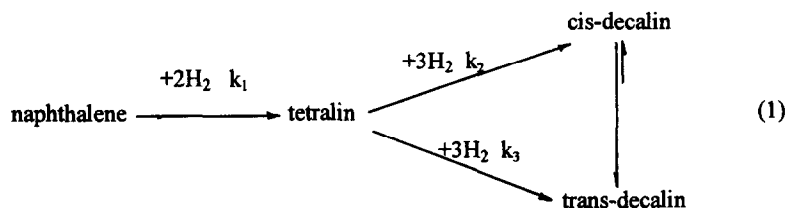
There are three different kinds of hydrogenated products of naphthalene in this study for all catalysts. The reaction can be described as depicted in Scheme 1 [31].

For the comparison of the sulfur tolerances of Pt/γ-Al₂O₃ and Pt/Bx–Al₂O₃ catalysts, naphtha-

lene was completely saturated for all catalysts at temperature 533 K, pressure 5.17 MPa and LHSV 2.8 h⁻¹. When the reaction activity was stable (after starting reaction 400 min), the benzothiophene was added into the reaction system to test the sulfur tolerance of catalysts. The results are shown in Fig. 4.

As can be seen from Fig. 4, catalysts Pt/Bx–Al₂O₃ have much better sulfur tolerance than Pt/γ-Al₂O₃. The sulfur tolerance of catalysts follows the sequence: Pt/B16–Al₂O₃ > Pt/B32–Al₂O₃ > Pt/Al₂O₃. There are two reasons of higher sulfur tolerance of Pt/Bx–Al₂O₃ catalysts than Pt/Al₂O₃ catalyst. One is that the platinum metal distribution of Pt/Bx–Al₂O₃ catalysts in the pellet is more homogeneous than that of Pt/Al₂O₃ catalyst [32], as shown in Fig. 2 and Fig. 3. The other reason is that the acidity of Bx–Al₂O₃ support is higher than that of Al₂O₃ support.

According to Schultze and Koppitz [33], when a sulfur species S^z comes in close contact with a metal M (Pt), a charge or partial charge transfer of electrons is possible (depends on the difference of electronegativities between the metal substrate and the absorbate): M + S^z → M–S^(z+λ) + λe⁻. According to Barbier et al. [7], more acid support makes more electronic transfer from the metal to the support, and causes an electron-deficient character to appear on the metal which will reduce the aptitude for adsorbing an acceptor compound such as sulfur. This effect is more important on the small metallic particles than on the larger ones. Therefore, the noble metal catalyst with more acidity shows a higher thioresistance. The effect of boron on the relative strength of the acid sites is very pronounced [27]. In going from alumina to B20–Al₂O₃, the acid strength is increased fast.



Scheme 1.

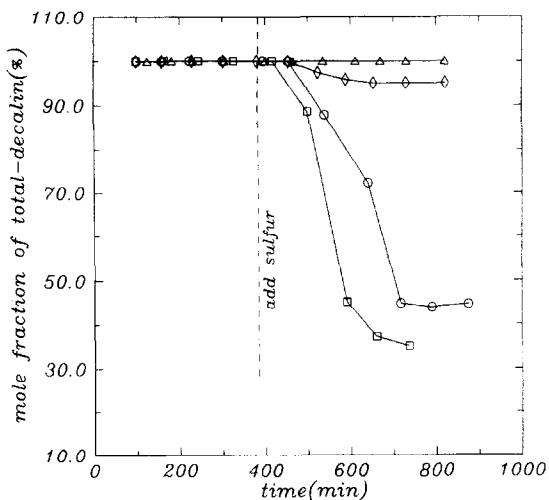


Fig. 4. The sulfur tolerance of Pt/Bx-Al₂O₃ catalysts. $P = 5.17$ MPa, LHSV = 2.8, H₂/oil = 1000 ml/ml. ○ Pt/Al₂O₃ ($T = 533$ K), □ Pt/Al₂O₃ ($T = 513$ K), △ Pt/B16-Al₂O₃ ($T = 513$ K), ◇ Pt/B32-Al₂O₃ ($T = 513$ K).

However, further increase in boron content do not increase the acid strength of the support. That is why Pt/Bx-Al₂O₃ catalysts show a higher sulfur tolerance than Pt/ γ -Al₂O₃ and Pt/B16-Al₂O₃ is more sulfur tolerance than Pt/B32-Al₂O₃.

According to Lin and Vannice [34], the aromatics adsorbed on acid sites in the metal-oxide interfacial region could react with hydrogen spilled-over from the metal surface; consequently, more acid supports would give an additional contribution to the overall activity. The acid centers on the supports are active in decomposing benzothiophene by spill-over hydrogen from Pt. The participation of Pt in adsorbed benzothiophene is thus lowered. Therefore, the effect of sulfur compound adsorbed in Pt metal on the hydrogenation is reduced in the high acidity of Pt-catalyst. More researches are needed to study why the noble metal catalyst with more acidity have a higher thioresistance.

3.3. The effect of Pt metal distribution on the thioresistance of Pt/ γ -Al₂O₃ catalysts

The sulfur tolerances of Pt/ γ -Al₂O₃ catalysts with different metal distributions were compared

and the results are shown in Fig. 5. Cat-Eng is a commercial Pt/ γ -Al₂O₃ catalyst (0.5 wt% Pt, $D = \frac{1}{8}$ in. and $L = \frac{1}{8}$ in.) with a sharp shell Pt metal distribution. The catalyst Pt*/Al₂O₃ has a uniform Pt metal distribution, as shown in Fig. 2. The catalyst Pt/Al₂O₃ has an intermediate metal distribution between the above two catalysts, as shown in Fig. 2. The low hydrogenation rate of Cat-Eng catalyst is due to low Pt content and large catalyst size which may produce by-passing and channelling phenomena. All the thioresistance experiments of catalysts were tested at 533 K, 5.17 MPa and LHSV 2.8 h⁻¹.

The sulfur tolerance of catalysts follows the sequence: Pt*/Al₂O₃ > Pt/Al₂O₃ > Cat-Eng. When poisoning is caused by feedstock impurities that react both with the active component and the catalyst support, the reaction results of catalyst would be intermediate between shell and uniform poisoning [35]. According to the results of Basset [28], the catalyst Pt/Al₂O₃ prepared from impregnation of chloroplatinic acid still retains a significant amount of chloride ions which are able to increase the acidic properties of the carrier. An increase in chlorine content induces a decrease in the extent of sulfur adsorption [36]. According to Barbier et al. [7], for supported catalysts, the elec-

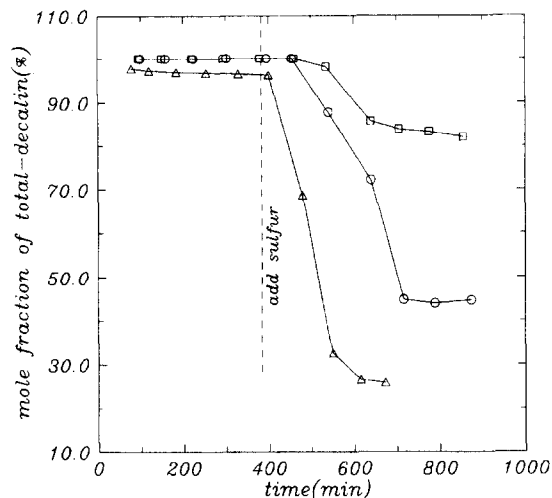


Fig. 5. The sulfur tolerance of Pt/Al₂O₃ catalysts with different metal distribution. $T = 533$ K, $P = 5.17$ MPa, ○ Pt/Al₂O₃, □ Pt*/Al₂O₃, △ Cat-Eng.

tronic state of metallic particles can be modified not only by the acidic properties of the support but also by the dispersion of the metal. The affinity of the catalysts for sulfur will be the result of these two phenomena. Vedrine et al. [37] and Foger and Anderson [38], using XPS data, pointed out that small platinum crystallites deposited on very acidic supports are electron deficient. When platinum is deposited on an acidic support, the support acidity effect plays a leading role and small platinum particles are more resistance to sulfur adsorption than the bulky catalysts. However without support effect, sulfur is preferentially adsorbed on platinum at sites of lowest coordination, such as ledge or edge sites, which are more numerous on small metallic particles [7]. When platinum is deposited on the same low-acidic support, by a compensation between size and support effect, the sulfur coverage will be almost the same, no matter what platinum dispersion there may be. Therefore, if the Pt metal distribution factor is negligible, the thioresistance of Pt/Al₂O₃ will be equal or a little higher than that of Pt*/Al₂O₃ catalyst due to the high metal dispersion and a little high acidity of Pt/Al₂O₃ catalyst.

If the poisoning by benzothiophene is uniform, the sulfur tolerance of Pt/Al₂O₃ will be equal or higher than Pt*/Al₂O₃. However the sulfur tolerance of Pt*/Al₂O₃ catalyst is higher than Pt/Al₂O₃, as shown in Fig. 5. The poisoning by benzothiophene of the catalyst would be a shell-like poisoning due to the low sulfur compound concentration in feed and high adsorption rate of benzothiophene. Therefore, an uniform Pt metal distribution over the catalyst shows a higher thioresistance than the white egg shell-type Pt metal distribution. Becker and Wei report the same results [32]. According to Fig. 4 and Fig. 5, Pt/B16–Al₂O₃ catalyst has better sulfur tolerance than Pt*/Al₂O₃ catalyst, although two catalysts have the same metal distribution. Therefore, the high thioresistance of Pt/B16–Al₂O₃ catalyst is not only due to homogeneous metal distribution in catalyst but also due to the high acidity of support.

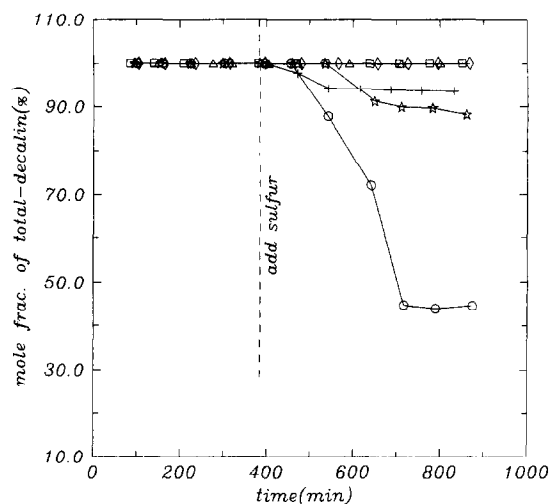


Fig. 6. The sulfur tolerance of Pt/AB_x and Pt/AB_xAP_y catalysts. P = 5.17 MPa, LHSV = 2.8 H₂/oil = 1000 ml/ml. ○ Pt/Al₂O₃ (T = 533 K), □ Pt/AB1 (T = 503 K), △ Pt/AB2 (T = 493 K), ◇ Pt/AB5 (T = 503 K), ☆ Pt/AB8 (T = 513 K), + Pt/AB5P10 (T = 513 K).

3.4. The thioresistance of Pt/AB_x catalysts

The sulfur tolerance of Pt/AB_x catalysts with different Al/B atomic ratio was compared and the results are shown in Fig. 6. The thioresistance of catalysts was tested at 5.17 MPa and LHSV 2.8 h⁻¹. The sulfur tolerance of catalysts follows the sequence: Pt/AB1 ≥ Pt/AB2 ≥ Pt/AB5 > Pt/AB8 > Pt/Al₂O₃. Experimental results showed that the sulfur compound not only poisoned the hydrogenation activity but also hydrogenolysis. Somorjai [39], Maurel et al. [40], and Apeste-guia et al. [41] proposed that hydrogenation (facile reaction) should be less affected by sulfur poisoning than hydrogenolysis (demanding reaction).

According to the results of Peil et al. [28] and Wang et al. [42], in going from pure alumina to an aluminum borate with a Al/B ratio of 20, the surface acid strength increases sharply. Further increase in boron content of support AB_x continually increases the acid strength, but a maximum strength was at low B/Al. Therefore, the hydrogenation activity of Pt/AB_x catalyst increased as the boron content of AB_x support increased [20].

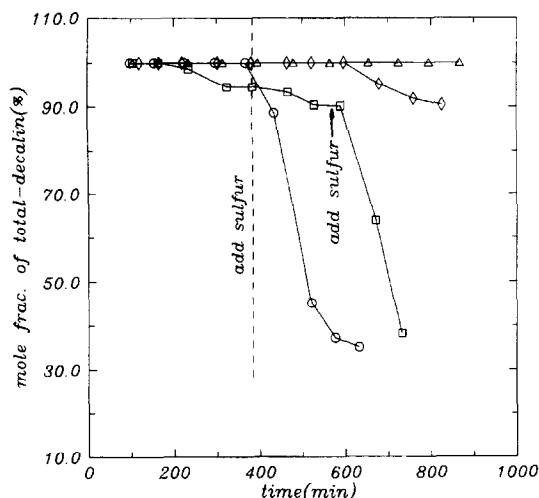


Fig. 7. The hydrogenation activity and sulfur tolerance of Pd/ABx catalyst. $T = 513$ K, $P = 5.17$ MPa, LHSV = 2.8, $H_2/\text{oil} = 1000$ ml/ml. \circ Pt/ Al_2O_3 , \square Pd/ Al_2O_3 , \triangle Pt/AB5 ($T = 503$ K), \diamond Pd/AB3.5.

According to all results mentioned above, the noble metal catalyst on a more acidic support is more thioresistant. Therefore, our experimental results are reasonable.

The hydrogenation activity of Pt/ABxAPy is as good as of the Pt/ABx catalyst, and its sulfur tolerance is also good, as shown in Fig. 6.

3.5. The hydrogenation activity of Pd/ABx catalyst

To check whether ABx support can be applied to prepare Pd-catalyst, Pd/ABx (1.0 wt% Pd) catalyst was prepared and its hydrogenation activity and sulfur tolerance were compared with that of the Pt/ABx and Pd/ Al_2O_3 catalysts, as shown in Fig. 7. It is shown that Pd/AB3.5 catalyst has a higher hydrogenation activity and sulfur tolerance than Pd/ Al_2O_3 catalyst. Chou and Vannice [43] report the same results, namely that the higher the acidity of support, the higher the hydrogenation activity of Pd-catalyst. The higher sulfur tolerance of catalyst Pd/ABx can be explained by the same ideas as with the catalysts Pt/ABx and Pt/Bx- Al_2O_3 . However, the hydrogenation activity and sulfur tolerance of Pd/ABx is not so good as of Pt/ABx, as shown in Fig. 7. The same results are obtained in the sense that the hydrogenation

activity and sulfur tolerance of Pt/ Al_2O_3 is better than that of Pd/ Al_2O_3 , as shown in Fig. 7. Also Koussathana et al. [44] reported that platinum is the most active metal for hydrogenation of aromatic compounds, what is obviously confirmed here.

3.6. The effect of temperature on the thioresistance

The sulfur resistance of catalyst depends upon reaction conditions, such as temperature and poison concentration. The effect of temperature on the sulfur tolerance of Pt/ Al_2O_3 and Pt/AB2 is shown in Fig. 4 and Fig. 8, respectively. These experimental results show that reaction temperature plays an important role in determining the sensitivity of catalysts to poisons. Generally, an increase in temperature will favor reversible adsorption and thereby increase sulfur tolerance of a given catalyst [21]. Berthier et al. [45] and Heegemann et al. [46] obtained the same result that more sulfur was adsorbed at lower temperature than at higher temperature. The actual steady-state activity in the presence of poisons may change appreciably with increasing temperature. This depends upon the degree of reversibility with respect to the adsorption of poison.

The selectivity of *cis*-decalin is increased when the benzothiophene is added into the reaction system, as shown in Fig. 8. There are two reasons for the increase of the selectivity of *cis*-decalin. One is the decrease of hydrogenation reaction rate and further the fact that a small amount of *cis*-decalin isomerizes to *trans*-decalin [31]. The other possible reason is that the isomerization reaction of *cis*-decalin may be more sensitive to the sulfur poison than hydrogenation reaction.

3.7. The effect of sulfur concentration in the feed on the sulfur tolerance

The effect of sulfur concentration on the sulfur tolerance of catalyst was studied at 503 K and 5.17 MPa over Pt/AB5 catalyst. As can be seen from Fig. 9, a high benzothiophene content in feed ren-

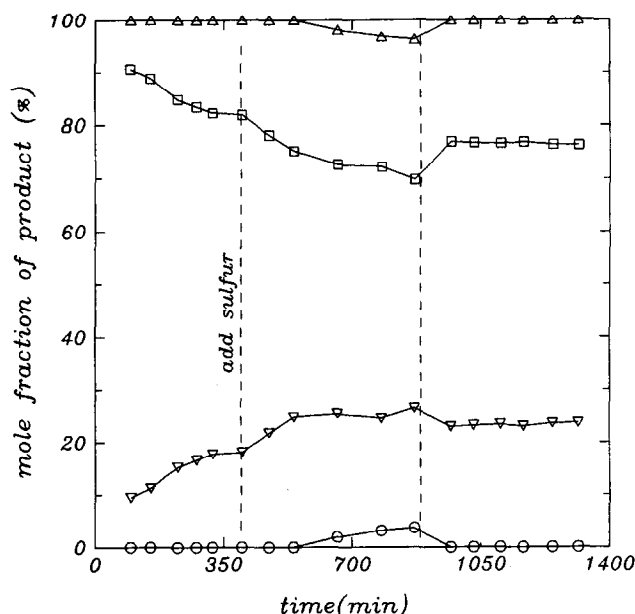


Fig. 8. The effect of temperature on the sulfur tolerance of Pt/AB2 catalyst. $T=493$ K at time < 880 min, $T=503$ K at time > 880 min. $P=5.17$ MPa, LHSV = 2.8, H_2 /oil = 1000 ml/ml. \circ Tetralin, ∇ cis-decalin, \square trans-decalin, Δ total decalin.

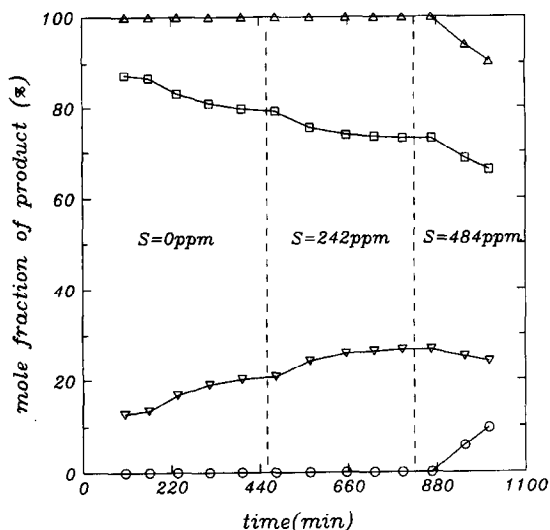


Fig. 9. The effect of sulfur concentration on sulfur tolerance of Pt/AB5 catalysts. $T=503$ K, $P=5.17$ MPa, LHSV = 2.8 hr^{-1} , H_2 /oil = 1000 ml/ml. At $t=450$ min sulfur was added. \circ Tetralin, ∇ cis-decalin, \square trans-decalin, Δ total decalin.

ders more sulfur compounds to be adsorbed on the catalyst. Hence the rate of hydrogenation decreases with the increasing benzothiophene concentration in the feed.

The hydrogenation of naphthalene was tested at 513 K and 5.17 MPa over the Pt/ Al_2O_3 catalyst, as shown in Fig. 10. At 400 min initiation of the reaction, the reaction rate reached a steady state

and a large amount of benzothiophene was then introduced into the reaction system. The hydrogenation rate decreased sharply where after the input of the sulfur compound was stopped. The rate of naphthalene hydrogenation recovered slowly, and finally the rate was only slightly lower than in the initial steady state, as shown in Fig. 10. The unsaturated compounds (aromatics) are able,

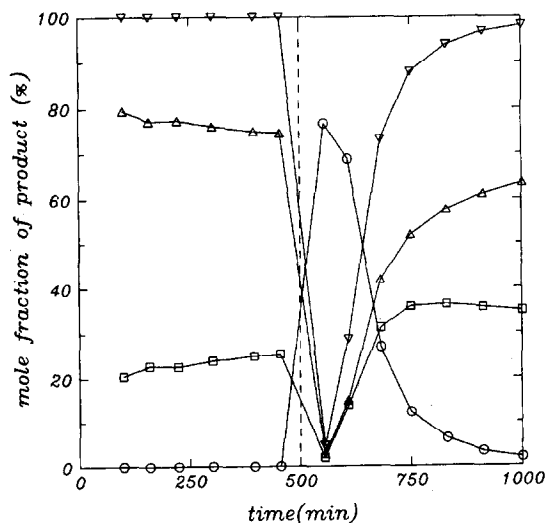


Fig. 10. The effect of sulfur concentration on sulfur tolerance of Pt/ Al_2O_3 catalyst. $T=513$ K, $P=5.17$ MPa and LHSV = 2.8. At $t=500$ min sulfur was added, and then stopped. \circ Tetralin, \square cis-decalin, Δ trans-decalin, ∇ total decalin.

due to their high heat of chemisorption, to displace reversible adsorbed sulfur compound and to recover themselves the hydrogenation activity. However, some sulfur compound remains irreversibly adsorbed on the catalyst [47]. Therefore, the hydrogenation activity cannot be completely returned to its initial steady state.

4. Conclusion

The Pt/AB_x and Pt/B_x-Al₂O₃ catalysts have higher hydrogenation activity and sulfur tolerance than Pt/γ-Al₂O₃, most likely due to the higher acidity of supports. When boron was added to Pt/γ-Al₂O₃ catalyst, it improved the catalyst hydrogenation activity and its thioresistance. The higher the boron content in the Pt/B_x-Al₂O₃ catalysts, the higher are the hydrogenation activity and sulfur tolerance of catalysts, although it is not a linear increase.

For the Pt/AB_x catalyst, the higher the boron content in the catalyst, the higher are the hydrogenation activity and sulfur tolerance. Pd/AB_x catalysts have also a higher hydrogenation activity and sulfur tolerance than Pd/γ-Al₂O₃ catalysts again due to the higher acidity of AB_x supports. However, Pd/AB_x catalysts have a lower hydrogenation activity and thioresistance than the Pt/AB_x catalysts.

The Pt metal distribution in catalyst influences the sulfur tolerance of Pt/γ-Al₂O₃ catalyst. A uniform Pt metal distribution of catalysts have a higher sulfur tolerance than the egg white shell-type Pt metal distribution. The poisoning by benzothiophene appeared to be like shell poisoning. Experimental results show that as expected more sulfur compound is adsorbed on the catalysts at lower temperatures and higher sulfur compound concentrations.

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