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Enhanced Sulfur Tolerance of Bimetallic PtPd/Al_2O_3 Catalysts for Hydrogenation of Tetralin by Addition of Fluorine

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Abstract A series of mono- and bi-metallic Pt-Pd/Al_2O_3 samples with and without F were studied as aromatic hydrogenation catalysts. The effects of changing the order of impregnation of the Pt precursor and F as well as varying the calcination temperature (300–500 °C) were investigated. Temperature programmed reduction (TPR) results demonstrate the presence of a higher fraction of dispersed metal precursor species left on the surface from the impregnation (PtO_xCl_y) on the Pt/Al_2O_3 sample calcined at high temperature. The impregnation of F before the Pt precursor significantly decreases the interaction between the metal and the support. However, this decrease is not observed when F is impregnated after the metal precursor. For the bimetallic Pt-Pd catalysts, the sample prepared adding F before the metal show a higher degree of Pt-Pd interaction than either the parent Pt-Pd/Al_2O_3 catalyst or the one prepared with F added later. TPD of ammonia result show the increase in strong acid sites when F is present. Activity tests for tetralin hydrogenation in the presence of 350 ppm dibenzothiophene indicate a better sulfur tolerance for all F-promoted catalysts, especially Pt-Pd.

Keywords Hydrogenation · Tetralin · Pt · Pd · F · TPR · Hydrogen chemisorption · XPS · TPD of NH_3

1 Introduction

There have been many attempts to upgrade different diesel fractions such as LCO by hydrogenation of polyaromatics. Catalysts that are typically used in industry for this upgrading are sulfided CoMo and NiMo catalysts, which have high sulfur tolerance and relatively low cost. However, these catalysts are not very active so high temperatures are required for the process. Thermodynamically, higher temperatures result in lower equilibrium conversions, so higher pressures are needed. During the last decade, studies have focused on noble metal catalysts which exhibit high activity at milder conditions [1–14]; however, the weakness of these catalysts is their sensitivity to the sulfur compounds present in the feed. In most studies, platinum-based catalysts have been employed with a second metal as a promoter (e.g., Pd, Ge, Cu, Ru) over different supports (e.g., alumina, silica-alumina, zeolite). The purpose of most of these studies has been to understand the deactivation by sulfur and improve the catalytic performance in the presence of sulfur. Many reports [6–9, 11–13] have demonstrated the superior sulfur tolerance of bimetallic Pt-Pd, compared to that of a monometallic Pt catalyst, particularly when prepared on acidic supports such as zeolites. The explanation of this tolerance has generally been associated to the electron deficiency generated in the metal by the acid support, thus inhibiting the formation of metal sulfide. Recently, Williams and coworkers [15] reported the increased tetralin hydrogenation by increasing the intermediate electronegativity of the supports. However, too much acidity could result in hydrogenation selectivity losses [3]. The incorporation of an electronegative atom, e.g., F, can be used to adjust the acidity of the catalyst support, i.e., alumina, as F replaces the surface hydroxyl group [16]. Several papers have

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reported the benefit of adding F to noble metal catalysts for different applications, e.g., oxidation [17], hydroisomerization [18], and hydrodechlorination [19]. Only a few patents have reported the use of F to promote aromatic hydrogenation in the presence of sulfur [20–22]. In our previous study [14], we reported that the F-promoted PtPd/Al_2O_3 was more active in the presence of a sulfur compound than the unpromoted catalysts. It was shown that the incorporation of F increased the acidity of the catalyst even though the Pt dispersion was relatively lower than that of the unpromoted catalyst. In that study, we noticed that several parameters in the catalyst preparation, including calcination temperature and order of impregnation, had a great impact on the physical properties and catalytic activity. Therefore, it is interesting to find the optimal preparation parameters for the F-promoted PtPd/Al_2O_3 catalyst and to understand the surface behavior of the catalyst. In this paper, we prepared a series of mono- and bi-metallic PtPd catalysts by varying calcination temperature and order of impregnation between the metal and F. The catalysts were characterized by temperature programmed reduction (TPR), hydrogen chemisorption, X-ray Photoelectron Spectroscopy (XPS) and tested for their activity in tetralin hydrogenation in both sulfur-free and 350 ppm sulfur-containing systems.

2 Experimental

2.1 Catalyst Preparation

Three pairs of mono- and bi-metallic PtPd catalysts were prepared by conventional incipient wetness impregnation (IWI). In each pair, fluorine was added either before or after the metal. In all cases, the support was gamma alumina (surface area of 274 m^2/g, pore volume of 1.11 mL/g, and pore diameter of 104 Å) provided by Saint Gobain NorPro Corporation. The alumina was first ground and sieved to 40–70 mesh. Impregnating solutions were prepared with hydrogen hexachloroplatinate hydrate ($H_2PtCl_6.6H_2O$, Acros, 40% Pt) dissolved in deionized water, and palladium chloride ($PdCl_2$, Carlo, 59.5% Pd) dissolved in concentrated hydrochloric acid. The metal loadings were adjusted in order to keep the same total metal molar fraction in all catalysts. Specifically, 1.6% Pt/Al_2O_3, 0.8%Pd/Al_2O_3, and 0.4% Pt-0.6% Pd/Al_2O_3 were prepared with and without 3 wt% F by varying the calcination temperature (300–500 °C) and order of impregnation of metal and F. After impregnation, the catalysts were dried under ambient conditions for 4 h, then dried overnight in an oven at 110 °C, and finally calcined in a furnace at a specified temperature using a heating rate of 10 °C/min for 2 h. The addition of ammonium hydrogen difluoride was conducted in the same manner as the metal, using deionized water as a diluent. The different catalysts prepared and their abbreviation names are listed in Table 1. The metal contents in wt% (±0.02), as measured by an atomic absorption spectrophotometer, are listed for each catalyst.

2.2 Catalyst Characterization

2.2.1 Temperature Programmed Reduction (TPR)

Temperature programmed reduction was carried out in a 1/4″ O.D. quartz reactor. Prior to the test, 50 mg of catalyst was packed in the reactor. For Pd and PtPd catalysts, dry

Table 1 List of catalysts with TPR and chemisorption analysis

Catalyst	Calcination temperature (°C)	%Pt	%Pd	%F	Order of impregnation	TPR: total H_2 consumption (a.u.)[a]	TPR: dispersive phase Pt/bulk phase Pt (IV/II + III)[b]	H:M	CO:M
Pt300	300	1.6			Pt	1.00	1.77	0.52	
Pt400	400	1.6	–	–	Pt	1.21	1.85	0.60	
Pt500	500	1.6	–	–	Pt	1.50	2.00	0.67	0.51
PtF500	500	1.6	–	3	F, Pt			0.99	0.80
FPt500	500	1.6	–	3	Pt, F			0.65	0.51
Pd500	500	–	0.8	–	Pd			0.34	
PdF500	500	–	0.8	3	F, Pd			0.19	
FPd500	500	–	0.8	3	Pd, F			0.20	
PtPd500	500	0.4	0.6	–	Pt-Pd			0.31	
PtPdF500	500	0.4	0.6	3	F, Pt-Pd			0.34	
FPtPd500	500	0.4	0.6	3	Pt-Pd, F			0.14	

[a] Total hydrogen consumption (arbitrary unit) during the course of TPR

[b] Ratio of hydrogen consumption for the reduction of dispersive phase platinum to that of bulk phase platinum

ice was used to cool the sample to 10 °C since PdO is an easily reducible oxide, even at room temperature. The TPR profiles were obtained by passing 5.0% H_2/Ar through the sample and waiting until the signal was stable for 20 min before heating the catalyst. The TPR runs were performed with a heating rate of 10 °C/min to 700 °C. The effluent gas was passed through a moisture trap and detected on-line by an SRI thermal conductivity detector.

2.2.2 *H_2 and CO Pulse Chemisorption*

Hydrogen and CO chemisorption was performed in the same apparatus as the TPR. Prior to the experiment, 50 mg of the catalyst was reduced with hydrogen at 300 °C for 1.5 h, to convert the metal oxide into metallic metal, and was then purged by nitrogen at 300 °C for 0.5 h and cooled to room temperature, after that it was pulsed with hydrogen gas to the reduced catalyst at 25 °C. The remaining gas was monitored by an SRI thermal conductivity detector. The metal dispersion, in terms of hydrogen (or CO)-to-metal molar ratio, was calculated based on the moles of gas adsorbed on the catalyst. Pulses of 20 μL H_2 and 500 μL of 3%CO in He were used for hydrogen and CO chemisorption, respectively.

2.2.3 *Temperature Programmed Desorption of Ammonia*

The acidity of the catalysts was analyzed by temperature programmed desorption of ammonia (TPD-NH_3). A total of 60 mg of catalyst was placed in a quartz reactor and reduced under H_2 flow (23 mL/min) at 300 °C for 1 h. The reactor was then cooled down to 100 °C under a flow of He. The adsorption of ammonia was carried out at this temperature with a flow of 1.0% NH_3/He (19 mL/min). At this point the physisorbed ammonia was purged by a flow of He (25 mL/min) for 1 h. The sample was then linearly heated to 650 °C under the He flow. The desorption of ammonia was analyzed on-line by a Varian® 3800 TCD detector as a function of temperature.

2.2.4 *X-ray Photoelectron Spectroscopy (XPS)*

The atomic surface composition of the calcined catalysts was analyzed by XPS technique. X-ray photoelectron spectra were acquired with an Alpha 110 Thermo electron spectrometer with a hemispherical digital electronics analyzer, model 8017, with monochromatic Mg Kα (energy ~ 1253.6 eV) X-ray source. The binding energies (BEs) of Pd 3 d, O 1s, F 1s, Al 2p, and Cl 2p were referenced to the C 1s peak at 290 eV. This reference gave BE values with a precision of 0.1 eV. Atomic surface contents were estimated from the areas of the peak, corrected using the corresponding sensitivity factors.

2.2.5 *Atomic Absorption Spectroscopy (AAS)*

The actual amounts of platinum (Pt) and palladium (Pd) loading in the prepared catalysts were determined by atomic absorption spectroscopy. The standard solutions of 1,000 ppm of Pt and Pd used in this work are manufactured by Merck. Firstly, a known weight of around 0.15 g of a catalyst were digested in freshly mixing concentrated nitric acid and concentrated hydrochloric acid, usually in a volumetric ratio of one to three (Aqua Regia) overnight. The solution was then diluted to the measuring range. The concentrations of Pt and Pd were obtained by comparing the solution's absorbance with the calibration curve of the standard solution. A Varian Spectra AA-300 was employed to determine the compositions of Pt and Pd in the catalysts prepared.

2.3 Catalytic Activity Testing

The feed in this study contains 25% tetralin (1, 2, 3, 4-tetrahydronaphthalene, TL, Acros, 97+%) and 75% dodecane. In the case of sulfur-containing feed, a calculated amount of dibenzothiophene (DBT; Aldrich, 99%), in order to get 350 ppm sulfur, was added to the feed mixture. The catalytic activity measurements were carried out in a continuous fixed-bed stainless steel 3/4″ O.D. reactor equipped with a thermowell to insert the thermocouple into the center of the catalyst bed. The catalytic activity was measured at a temperature of 300 °C with a total pressure of 500 psig, H_2/HC molar ratio of 11, and LSV of 100 h^{-1}. In each test, 40 mg of catalyst was used. The catalyst was reduced under a flow of H_2 at 500 psig for 2 h. After the pretreatment, the feed was introduced into the reactor using an Everseiko high-pressure pump. The products were trapped by cooling water and analyzed online by an HP6890 gas chromatograph with FID using an HP-5 column (diameter, 0.318 mm; length, 30 m).

3 Results and Discussion

3.1 Catalyst Characterization

3.1.1 *Hydrogen/CO Chemisorption*

The metal dispersion of the prepared catalyst analyzed by hydrogen chemisorption is shown in Table 1. For comparison, some catalysts were also tested for CO chemisorption. The results showed that the Pt catalyst had the highest metal dispersion, in terms of H (or CO)-to-metal ratio, compared to the Pd and bimetallic Pt-Pd catalysts. For the Pt catalysts, it was found that those calcined at 500 °C gave a better metal dispersion than those calcined at lower temperatures. Considering the order of impregnation, the sample prepared by adding F before the metal exhibited much higher Pt dispersion than either the catalyst with no F or the catalyst prepared by adding F after the metal. The CO chemisorption on these catalysts showed the same trend as those obtained by hydrogen chemisorption. This result is in agreement with previous studies [17, 18] showing better metal dispersion when Pt was added to fluorinated alumina. However, we found that adding F either before or after lowered the metal dispersion when the catalysts were calcined at 350 °C [14]. This demonstrates the great effect of calcination temperature. For the Pd catalysts, the addition of F had an adverse effect on the metal dispersion. For the PtPd catalysts, like Pt, the metal dispersion was increased when the metals were impregnated on fluorinated alumina. By contrast, the dispersion was decreased when F was added after the PtPd. This is possible that the metals can easily agglomerate during the NH_5F_2 calcination, where oxidation and reduction occur simultaneously.

3.1.2 Temperature Programmed Reduction (TPR)

Figure 1 shows the TPR profiles for all the Pt catalysts. Three main peaks were observed in all cases. Since hydrogen hexachloroplatinate was used as the platinum precursor, the first two peaks located at 200 and 240 °C (II and III) can be referred to as the reduction of three-dimensional bulk phase of oxy- or hydroxychlorinated platinum while the high temperature peak located at 360 °C (IV) is referred to the reduction of the two-dimensional dispersive oxychlorinated platinum [23–25].

In agreement with previous reports [23], a strong interaction between Pt and the alumina support is evident when the Pt loading is lower than 3%. That is, the PtO_xCl_y precursor should be decomposed by a 400 °C reduction in hydrogen [26], i.e.,

$$PtO_xCl_y + (x + 0.5y)H_2 \rightarrow Pt + xH_2O + HCl.$$

Subsequently, the reduced platinum can be further converted to platinum oxide by oxidation with oxygen. In agreement with the report, the reduction of platinum oxide species was observed on the Pt500 catalyst re-oxidized at 500 °C for 2 h, as indicated by a peak located at 130 °C (Fig. 1, peak I). By increasing the calcination temperature from 300 °C to 500 °C, the total hydrogen consumption, as shown in Table 1, increased, which corresponds to the increase in metal dispersion. Noticeably, the ratio of the dispersive phase to bulk phase (IV/II + III) increased with calcination temperature. Moreover, the reduction temperature of the highly dispersed PtO_xCl_y species was shifted to higher temperature, indicating the stronger metal/support interaction of the sample calcined at high temperature.

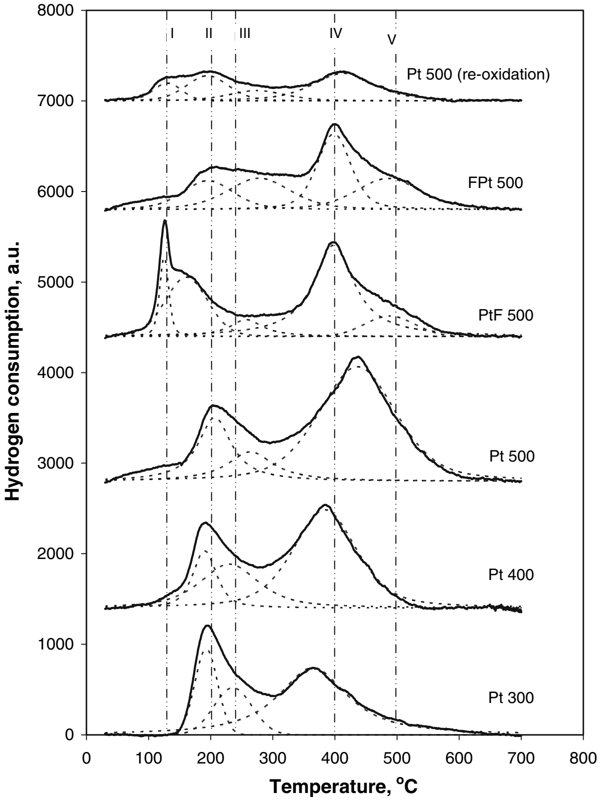

Fig. 1 Temperature programmed reduction of Pt/Al_2O_3 catalysts with and without F prepared at different calcination temperatures and orders of impregnation

In the presence of fluorine, the TPR profiles were significantly different between the two orders of impregnation. The one prepared by adding F after (FPt500) had a profile similar to the non-F catalyst (Pt500) but the peak at 200 °C was reduced. It is possible that part of the two-dimensional bulk phase PtO_xCl_y has been reduced during the calcination of NH_5F_2 in the F-impregnating step. For the one prepared by fluorination alumina first (PtF500), the reduction of platinum oxide at 130 °C (I) was clearly observed. This could be due to the fact that F has replaced oxygen or the hydroxyl group on the alumina surface; thus, the formation of the oxy- or hydroxyl-chlorinated platinum species was partially limited. The peak at 150 °C could correspond to the reduction of the PtO_xCl_y species, which is catalyzed by reduced platinum oxides. For both FPt500 and PtF500, the hydrogen consumption at 500 °C was observed. This could refer to the reduction of fluorinated platinum species.

Figure 2 is a comparison of the TPR profiles of Pt500, Pd500, PtPd500, FPtPd500, PtPdF500, and PtPdCl500 catalysts. In the TPR of the Pd500 catalysts, there are two reduction peaks; the PdO was reduced at below 100 °C and the PdO_xCl_y was reduced at 120 °C. The TPR of bimetallic PtPd500 had peaks similar to the monometallic catalysts. However, it is not simply the summation of the monometallic catalysts. This could be due to some interaction between the two metals. This kind of modification was previously observed when the second metal was present [6, 14]. However, the peak at around 430 °C, which corresponds to the strong interacting PtO_xCl_y species, was still present. For the FPtPd500 catalyst, the TPR profile was similar to the one without F, but the peak due to the metal oxide species (the peak below 100 °C) disappeared. This was because the metal oxide species were reduced during the calcination of NH_5F_2 at the F addition step. Interestingly, PtPdF500 catalyst showed a much narrower distribution with no PtO_xCl_y species observed. This result indicates a stronger Pt-Pd interaction on the PtPdF500 over other catalysts. For comparison, PtPdCl500 was prepared in the same manner as PtPdF500 using NH_5Cl_2 as a chlorine precursor. The TPR profile of the PtPdCl500 was similar to the PtPdF500. This pointed out that F and Cl exhibited similar behavior in modifying the surface. As we have shown in Fig. 1 for Pt catalysts, the interaction of Pt and alumina is diminished when Pt is added to fluorinated alumina. This could result in the improved interaction between Pt and Pd in the bimetallic catalyst.

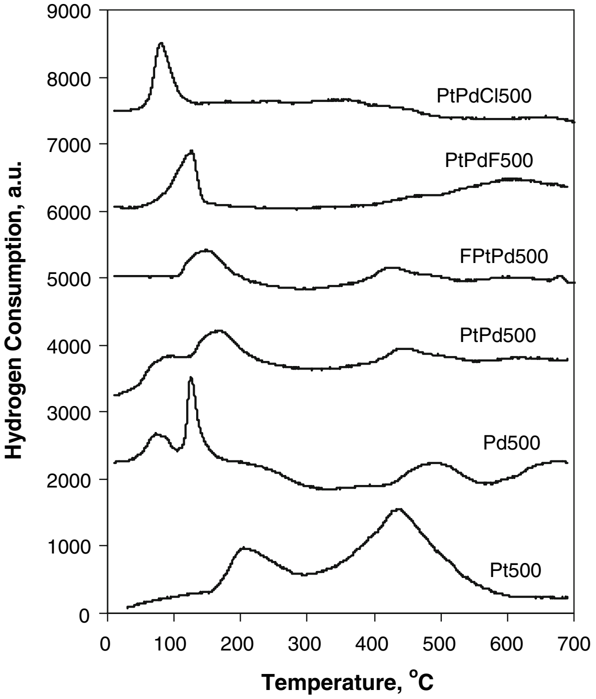

Fig. 2 Temperature Programmed Reduction of mono- and bi-metallic Pt-Pd catalysts calcined at 500 °C prepared with and without F and Cl

3.1.3 Temperature Programmed Desorption of Ammonia ($TPD-NH_3$)

The bimetallic Pt Pd catalysts with and without F were characterized for their acidity by TPD of ammonia technique. The TPD profiles are shown in Fig. 3. The profiles are categorized into three main groups. Low temperature peaks located in the temperature range of 100–320 °C can be ascribed to the ammonia adsorbed on the weakest acid sites. The peaks centered at 440 and 500 °C corresponded to the ammonia adsorbed on the intermediate and strongest acid sites, respectively. It has been reported that the Pt/Al_2O_3 catalyst prepared with chlorine-containing platinum precursors, i.e., $(NH_4)_2PtCl_4$ and $(NH_4)_2PtCl_4$), exhibited a higher acidity than the catalyst prepared by a non-chlorine precursor i.e., $Pt(NH_3)_4(OH)_2$ [27]. The TPD profiles in Fig. 3 clearly show the increase in acidity when F was added to the catalysts either before or after the metal. Noticeably, the catalyst prepared by adding F

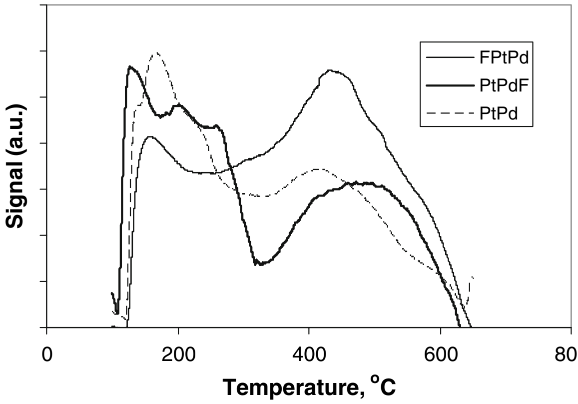

Fig. 3 TPD profiles of ammonia desorption of $PtPd/Al_2O_3$, $PtPdF/Al_2O_3$ and $FPtPd/Al_2O_3$ catalysts

Table 2 Atomic surface composition (mol%) of different calcined catalysts obtained by XPS analysis

Catalyst	O 1s	F 1s	Al 2p	Cl 2p	Pd 3d
Pd500	48.9	–	49.8	1.1	0.1
PdF500	47.5	3.3	46.6	0.6	0.3
FPd500	46.4	4.3	48.9	0.3	0.1
PtPd500	49.4	–	49.7	0.6	0.3
PtPdF500	45.5	5.1	48.9	0.3	0.2
FPtPd500	46.5	3.2	49.7	0.4	0.2

before metal (PtPdF) showed a lower fraction of medium and strong acid sites compared to the one prepared by adding metal before F (FPtPd). This could be due to the hydrolysis of F on the alumina surface which could occur in the presence of water during the second step of metal impregnation.

3.1.4 X-ray Photoelectron Spectroscopy (XPS)

Table 2 illustrates the atomic surface compositions of calcined Pd and PtPd catalysts as determined by XPS. As previously observed [14], the surface oxygen concentration decreased when F was present, as F partially replaced

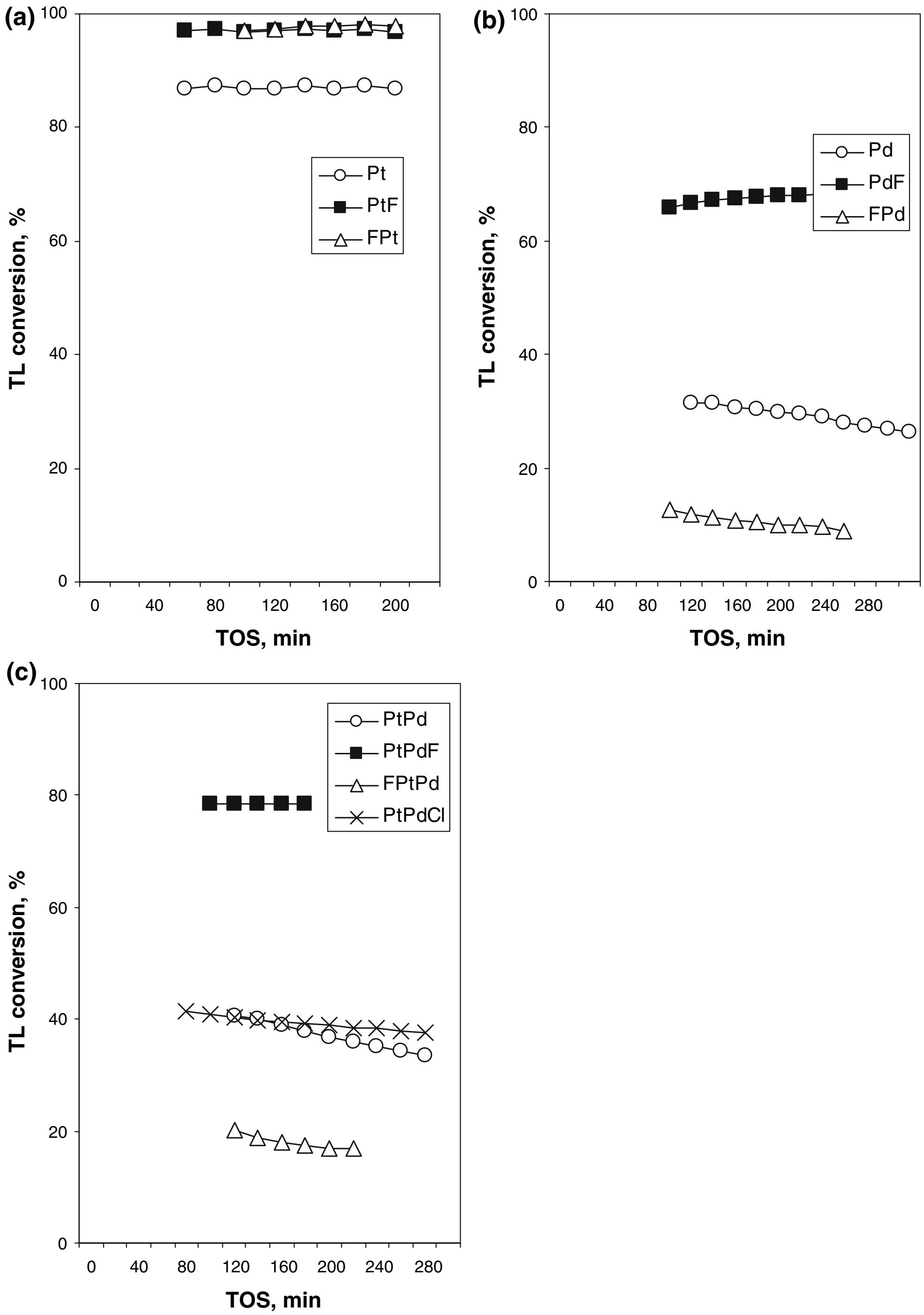

Fig. 4 Tetralin conversion as a function of timeon-stream in the absence of the S-compound. Reaction conditions: 300 °C and 500 psi, $H_2/HC = 11$, LHSV = 100 h^{-1}. (**a**) Pt/Al_2O_3 catalysts; (**b**) Pd/Al_2O_3 catalysts; (**c**) PtPd/Al_2O_3 catalysts

oxygen or hydroxyl groups on the alumina surface [16]. In agreement with the TPR result, the surface chlorine composition decreased as the metal chlorinated species decreased when F was added.

3.2 Catalytic Activity Measurements

3.2.1 Hydrogenation of Tetralin in the Absence of Sulfur

All of the catalysts were tested for their hydrogenation activity under the same reaction conditions using 25% tetralin in dodecane as a model feed. In the absence of sulfur, the conversion of tetralin as a function of time-on-stream over Pt, Pd, and PtPd catalysts are illustrated in Fig. 4a–c, respectively. The calculated TOFs at 4 h time-on-stream are summarized in Table 3. The platinum catalysts gave the highest tetralin conversion in the sulfur-free system compared to the other metal catalysts. In each catalyst pair, it was observed that the catalysts prepared by adding F before metal exhibited outstanding activity compared to the other catalysts in the same series. The addition of F after metal also gave a better conversion for Pt catalysts but this was not the case for the Pd and PtPd catalysts. Even though the PtPdCl500 had a similar TPR profile to the PtPdF500 catalyst, the PtPdCl500 did not give high tetralin conversion, as observed on the other. Considering specific activity, without F, the bimetallic catalyst had a comparable TOF to the monometallic catalysts. The addition of F significantly improved the TOF for the Pd and PtPd catalysts.

In the hydrogenation of tetralin, two isomers of decalin, *cis*-decalin and *trans*-decalin, are considered as main products. The isomers could determine the intermediate species and reaction pathway. As the *cis*-molecule is more flexible than the *trans*-molecule, *cis*-decalin is preferred for subsequent ring-opening reaction in order to boost up the cetane number for diesel fuel. As discussed earlier regarding the product selectivity over the catalysts cal at 350 °C [14], the trans/*cis*-decalin ratio was about unity for the Pt catalysts. The ratio was about three for the Pd and PtPd catalysts. That investigation was in agreement with the notion that in the PtPd catalyst, the Pd was located on top of the Pt so that the catalyst behaved like a Pd catalyst. In this work, the trans/*cis*-decalin ratio was plotted as a function of tetralin conversion (Fig. 5). The trans/*cis*-decalin ratio obtained on the Pt and Pd catalysts were 0.8 and 3.0, similar to what we found in the previous study [14, 28]. By contrast, the PtPd and PtPdF catalysts gave a trans/*cis*-decalin ratio of about 2.0, which is in between that of the Pt and Pd catalysts. Noticeably, the ratio obtained on the FPtPd was about 3.0, similar to that of the Pd catalyst. This trend demonstrates that catalyst preparation and pretreatment has a significant impact on the metal–metal or metal-support interaction, resulting in a different morphology and consequently a different product distribution.

Table 3 Turnover frequency of tetralin hydrogenation in the absence and in the presence of sulfur compound

Catalyst	Conversion at 4 h TOS (%)		TOF at 4 h TOS (s^{-1})	
	Sulfur-free	Sulfur	Sulfur-free	Sulfur
Pt400	71.9	1.0	5.853	0.084
Pt500	87.0	1.0	8.248	0.090
PtF500	97.0	4.2	6.140	0.265
FPt500	97.7	1.9	9.489	0.181
Pd500	29.1	0.8	5.925	0.157
PdF500	67.4	1.3	24.407	0.475
FPd500	10.6	0.8	3.571	0.254
PtPd500	37.0	0.9	8.219	0.189
PtPdF500	78.5	3.1	15.532	0.603
FPtPd500	18.1	1.6	8.880	0.806

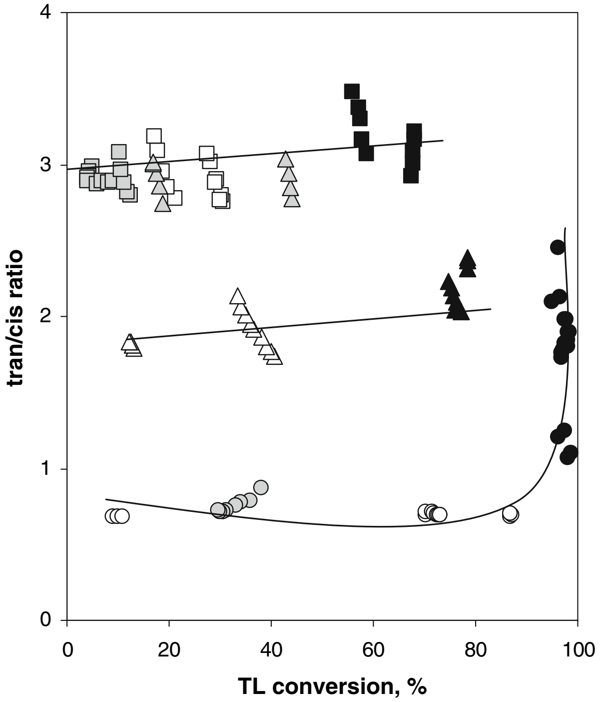

Fig. 5 Trans/*cis*-decalin ratio in the product of tetralin hydrogenation over different catalysts as a function of conversion. Reaction conditions: 300 °C and 500 psi, H_2/HC = 11, LHSV = 100 h^{-1}. Open circle = Pt catalysts with no F; gray circle = PtF catalysts; opaque circle = FPt catalysts; open square = Pd catalysts with no F; gray square = PdF catalysts; opaque square = FPd catalysts; open triangle = Pt-Pd catalysts with no F; gray triangle = PtPdF catalysts; opaque triangle = FPtPd catalysts

3.2.2 Hydrogenation of Tetralin in the Presence of 350 ppm Sulfur

In order to compare the sulfur tolerance of the catalysts, a 25% tetralin in dodecane feed containing 350 ppm S was employed, using dibenzothiophene as the sulfur compound. The conversion of tetralin as a function of time on stream over Pt, Pd, and PtPd catalysts is illustrated in Fig. 6a, b, and c, respectively. As expected, the conversion of tetralin declined in the presence of sulfur, but, in agreement with previous studies [2, 3, 5, 8, 9, 11–14, 29], the PtPd500 showed a higher TOF than either monometallic Pt500 or Pd500 catalysts (see Table 3). In most cases, the catalysts with F addition exhibited better conversion than the parent metal catalysts. While in the sulfur-free reaction the bimetallic PtPdF500 catalyst showed twice the TOF of the Pt500, it exhibited a much higher TOF (7 times) in the presence of sulfur. This indicates a significant improvement in sulfur tolerance by addition of Pd and F to the Pt catalyst. The FPtPd500 catalyst also exhibited a high TOF in the presence of sulfur. However, the conversion is rather low due to the low metal dispersion.

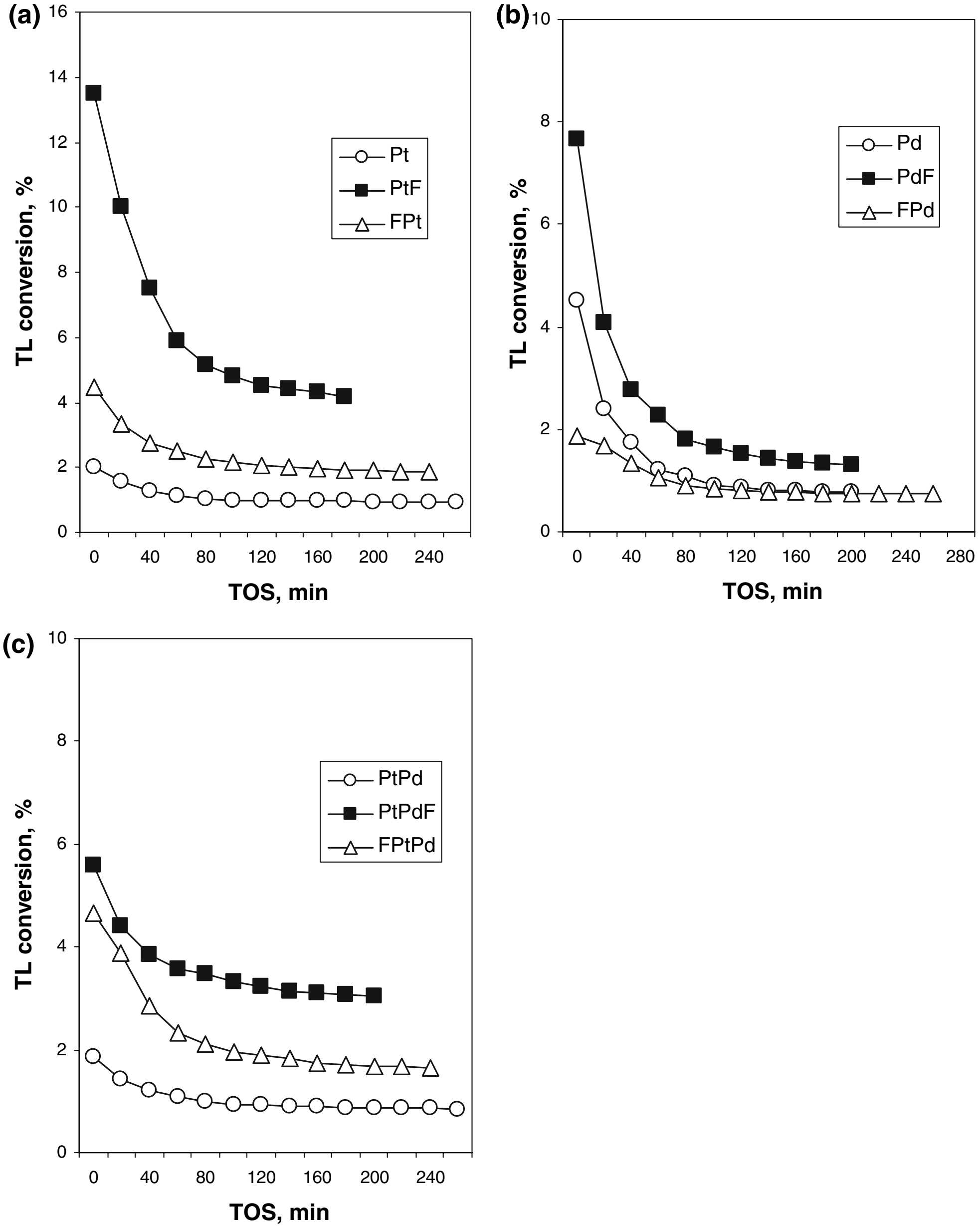

Fig. 6 Tetralin conversion as a function of time-onstream in the presence of 350 ppm S. Reaction conditions: 300 °C and 500 psi, H_2/HC = 11, LHSV = 100 h^{-1}. (**a**) Pt/Al_2O_3 catalysts; (**b**) Pd/Al2O3 catalysts; (**c**) PtPd/Al_2O_3 catalysts

4 Conclusions

The addition of F can increase the sulfur tolerance of Pt/Al_2O_3, Pd/Al_2O_3, and Pt-Pd/Al_2O_3 catalysts in tetralin hydrogenation. The difference in calcination temperature and order of impregnation has a significant impact on the surface acidity, metal/metal or metal/surface interaction, which can lead to different activity, product selectivity, and sulfur tolerance. The catalyst calcined at 500 °C exhibits a higher fraction of dispersed metal precursor over alumina than those calcined at lower temperatures. The addition of F before the metal can reduce the metal/support interaction by the reduction of oxy- or hydroxy-chlorinated species, which have a strong interaction with the surface; thus increasing the Pt-Pd interaction.

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References

1. Chiou J-F, Huang Y-L, Lin T-B, Chang J-R (1995) Ind Eng Chem Res 34:4277
2. Jan C-A, Lin T-B, Chang J-R (1996) Ind Eng Chem Res 35:3893
3. Yasuda H, Yoshimaru Y (1997) Catal Lett 46:43
4. Chang J-R, Chang S-L (1998) J Catal 176:42
5. Qian W, Yoda Y, Hirai Y, Ishihara A, Kabe T (1999) Appl Catal A 184:81
6. Navarro RM, Pawelec B, Trej JM, Mariscal R, Fierro JLG (2000) J Catal 189:184
7. Kabe T, Qian W, Hirai Y, Li L, Ishihara A (2000) J Catal 190:191
8. Guillon E, Lynch J, Uzio D, Didillon B (2001) Catal Today 65:201
9. Augusto CCC, Zotin JL, Faro AdC (2001) Catal Lett 75:37
10. Rousset JL, Stievano L, Cadete Santos Aires FJ, Geantet C, Renouprez AJ, Pellarin M (2001) J Catal 202:163
11. Fujikawa T, Idei K, Ohki K, Mizuguchi H, Usui K (2001) Appl Catal A 205:71
12. Pawelec B, Mariscal R, Navarro RM, van Bokhorst S, Rojas S, Fierro JLG (2002) Appl Catal A 225:223
13. Barrio VL, Arias PL, Cambra JF, Guemez MB, Pawelec B, Fierro JLG (2003) Fuel 82:501
14. Jongpatiwut S, Li Z, Resasco DE, Alvarez WE, Sughrue EL, Dodwell GW (2004) Appl Catal A 262:241
15. Williams MF, Fonfe B, Woltz C, Jentys A, van Veen JAR, Lercher JA (2007) J Catal 251:497
16. Ghosh AK, Kydd RA (1985) Catal Rev Sci Eng 27:539
17. Chuang KT, Davydov AA, Sanger AR, Zhang M (1997) Catal Lett 49:155
18. Ali A-GA, Ali LI, Aboul-Fotouh SM, Aboul-Gheit AK (2001) Appl Catal A 215:161
19. Early K, Kovalchuk VI, Lonyi F, Deshmukh S, d'Itri JL (1999) J Catal 182:219
20. White RJ, Houston RJ (1969) US Patent 3435085
21. Estes JH, Herbstman S, Kravitz S (1974) Britain Patent GB 1363179
22. Guillon E, Uzio D, Didillon B (1999) European Patent 955,090
23. Hwang C-P, Yeh C-T (1996) J Mol Catal A 112:295
24. Paulis M, Peyrard H, Motes M (2001) J Catal 199:30
25. Borgna A, Garetto TF, Apesteguia CR, Le Normand F, Moraweck B (1999) J Catal 186:433
26. Lieske H, Lietz G, Spindler H, Volter J (1983) J Catal 81:8
27. Paulis M, Peyrard H, Montes M (2001) J Catal 199:30
28. Dokjampa S, Rirksomboon T, Osuwan S, Jongpatiwut S, Resasco DE (2007) Catal Today 123:218
29. Yasuda H, Matsubayashi N, Sato T, Yoshimura Y (1998) Catal Lett 54:23