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Strong effect of transitional metals on the sulfur resistance of Pd/HY-Al$_2$O$_3$ catalysts for aromatic hydrogenation

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Abstract

In order to improve the sulfur resistance of noble metal catalysts in the aromatic hydrogenation of diesel fuel, the alloying effect of non-noble metals with Pd was studied. Toluene hydrogenation over Pd and Pd-M bimetallic catalysts (M = Cr, W, La, Mn, Mo, Ag) on a mixed HY-Al$_2$O$_3$ support was investigated in the presence of 3000 ppm sulfur as thiophene in the feedstock. The results showed that the addition of the second metals strongly affected the activity of toluene hydrogenation, which suggests that the sulfur resistibility of Pd-M bimetallic catalysts is much different from single Pd. La, Mn, Mo and Ag decreased the sulfur resistance of the palladium catalysts. For example, the toluene conversion at 553 K was observed to decrease sharply from 39.4 wt.% on Pd to 1.6 wt.% on Pd-Ag, which is by a factor of 25. One of the important findings in this article is that Cr and W increase hydrogenation activity of Pd catalysts. The reactions occurring on these catalysts include hydrogenation, isomerization and hydrocracking. The addition of the second metals has no noticeable effects on the hydrogenation and isomerization selectivity, but it slightly suppresses hydrocracking reactions. The four typical catalysts, Pd-Cr, Pd-W, Pd-Ag and Pd were characterized by infrared (IR) spectroscopy of pyridine and CO. IR spectra of CO revealed the strong interaction between Pd and the second metal as Cr, W and Ag (or their oxide), indicating that the improvement in sulfur resistance originates from electron-deficient Pd with the addition of second metals. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

A high aromatic content in diesel fuel will lower its cetane number and contribute significantly to the formation of undesired emissions in the exhaust gas. As a result of stringent environmental regulations, to lower the aromatic content in diesel fuel by hydrogenation is becoming one of the most important technologies in petroleum refining industry [1–3]. Aromatic hydrogenation, specifically for monoaromatics, is more difficult than hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) on conventional sulfide catalysts [2]. In addition to a high activation energy (ca. 92 kJ/mol) on Ni-W-S/Al$_2$O$_3$, also thermodynamics limits the yield of aromatic hydrogenation within the normal operating range of hydrorefining. Therefore, the deep hydrodearomatization (HDA) is a very challenging task by conventional hydrotreating technology using supported Ni(Co)Mo(W) sulfide catalysts.

Two-stage hydrotreating routes have been recommended to achieve low levels of aromatics [4,5]. In

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the two-stage process, a sulfide catalyst is used in the first stage to reduce sulfur and nitrogen, and a noble metal catalyst is used in the second stage for aromatic hydrogenation. On the one hand, this process is highly effective on the deep reduction of aromatics due to the inherent high hydrogenation activity of noble metals, but on the other hand, noble metals are very sensitive to sulfur poisoning. Severe first stage hydrotreating conditions (high hydrogen pressure, low weight hourly space velocity (WHSV)) would be required to meet the second stage feedstock sulfur specifications of less than 10 ppm. This would increase the investment on facilities and operating costs. Consequently, the sulfur resistance of noble metal catalyst is significant for the two-stage process.

Platinum or palladium is frequently used as active components in such catalysts. Pd is not only the active metal for aromatic hydrogenation, but also more sulfur-resistant than Pt [6]. Therefore, we selected Pd as the main active component in our catalyst.

The sulfur resistance of a noble metal catalyst can be improved by an acidic support, such as amorphous $SiO_2-Al_2O_3$, $B_2O_3-Al_2O_3$, or acidic zeolites [7–14]. The high sulfur resistance of Pt or Pd on an acidic support arises from the formation of electron-deficient metal particles, $M^{\delta+}$, because of the interaction of metal particles with the Bronsted acid sites [15–17]. The sulfur resistance of electron-deficient metal particles is suggested to come from the small bonding energy of the electron acceptor sulfur atoms with the electron-deficient Pt or Pd clusters that act as the electron donor [16,17].

The reactions occurring over the noble catalyst on acidic support include hydrogenation (or saturation), isomerization, hydrogenolysis (hydrocracking). Among these reactions, the excessive hydrocracking should be avoided because it leads to yield loss and increases hydrogen consumption.

In this paper, the catalyst support is a mixture of Y-type zeolite and alumina. Zeolites, especially Y-type zeolites, provide more possibilities than other supports to adjust the acidity, pore structure, and other properties. Therefore, Y-zeolite supported noble metal catalysts have received increasing attention in recent years as important industrial catalysts for aromatic hydrogenation [1–3,18]. Although, Y-zeolites are excellent supports, the pure zeolite cannot be used due to its poor mechanical strength. One or more components are added, such as Al_2O_3, which mainly act as binder and also improve the pore distribution of support.

Another possibility to improve sulfur resistance is to alloy the active component with another metal. Sachtler and Van Santen [19] reviewed the catalytic properties of alloys, and stated that bimetal and multimetal catalysts exhibit different activity, selectivity and stability from their monometal counterparts. Because Pt-Pd on various supports exhibits higher sulfur tolerance than either of the components, many researchers were attracted by this system [20–27]. Although, both Pt and Pd are expensive noble metals, few papers dealing with the sulfur-resistance of bimetallic catalysts with compositions other than Pt-Pd can be found [1,2]. Recently, Fujikawa et al. [27] studied the sulfur resistance of Pt-M/$SiO_2-Al_2O_3$ system (M = Pd, Re, Sn, Ir, Ni, Mo, Ge, etc.) using hydrotreated light cycle oil (LCO)/straight-run light gas oil (SRLGO) feed, and found the addition of second metal had no positive effect on hydrogenation activity or sulfur resistance of Pt except for Pt-Pd bimetallic combination. So far, except for Pd-Pt, no positive alloying effects on sulfur resistance of noble metal catalyst for deep aromatics hydrogenation were reported in the literatures.

In order to further investigate the possibility to enhance sulfur resistance of noble metal catalyst for aromatic hydrogenation of diesel fuel, a variety of Pd-M/HY-Al_2O_3 bimetallic catalysts, where M are non-noble transitional metal elements as Cr, Mo, W, La, Mn, Ag, were prepared. The sulfur resistance of these catalysts was tested with a mixture of toluene, thiophene and *n*-hexane (3000 ppm sulfur) under conditions similar to industrial hydrotreating. In this paper, our general aim is to report the strong effect of the second metals on the sulfur resistance of Pd catalysts. The effects of the second metal on the activity, selectivity and acidic properties are presented and the origin of the observed properties is discussed. It is surprising that some Pd-M bimetallic catalysts displayed much different sulfur resistance from single Pd one. One of the most significant findings in the article is that Cr and W noticeably increase the sulfur resistance of Pd catalysts, which was not reported. Infrared (IR) spectroscopy of chemisorbed CO was employed to investigate the electronic structure of Pd in an attempt to study the mechanism of sulfur resistance of bimetallic catalysts.

2. Experimental

2.1. Catalyst preparation

The precursor of HY in the catalysts is NH_4Y (produced by the Changling Catalyst Factory, China Petrochemical Corporation, SiO_2/Al_2O_3 = 5). The precursor of Al_2O_3 used in this study is pseudo-boehmitic powder (SB powder produced by Condea, surface area $238\,m^2/g$).

The support was prepared by the method of extrudation: 70 g NH_4Y was mixed with 30 g Al_2O_3, followed by kneading and extruding, and finally calcined at 873 K for 2 h.

The catalyst samples were prepared by pore volume impregnation of the support described above. The support was exposed to the solution of $Pd(NH_3)_4Cl_2$ in deionized water, followed by drying at 393 K for 2 h and calcination at 823 K for 2 h.

The second metal was introduced to the Pd catalyst by sequential pore volume impregnation. The Pd catalyst was impregnated with aqueous solutions of the corresponding salts for 2 h, followed drying at 393 K for 2 h, and then calcined at 823 K for 2 h. The precursors used for the preparation of the bimetallic catalysts are listed in Table 1.

The amount of each salt used in the impregnation was chosen to give catalysts with the same loading of Pd and the second metal. The compositions of the catalysts are summarized in Table 1.

2.2. Catalytic tests

The sulfur resistance of catalyst was tested with a continuous down flow fixed-bed reactor. The reactor was packed with 1.0 g catalyst (40–60 mesh) diluted with an inert 40–60 mesh ceramic in a ratio of 1:1. The upper and bottom part was filled with particles of a catalytically inactive ceramic material for preheating and preventing channel effects.

The catalysts were first reduced at 573 K under 4.2 MPa of pure hydrogen with a flow rate of 400 ml/min for 2 h. After reduction, the catalytic reactions were carried out with a WHSV of $4.0\,h^{-1}$ and flowing hydrogen (H_2/toluene molecular ratio = 40), under 4.2 MPa. The reaction temperature is in the range of 533–573 K. Reaction products were analyzed in-line by gas chromatography.

For sulfur resistance tests, the mixture of toluene and n-hexane in a volume ratio of 1:1 was used as feedstock, and thiophene was added to adjust a sulfur concentration of 3000 ppm.

Wall reactions and the hydrogenation activity of the catalyst were checked using a sulfur-free feedstock, which is the mixture of toluene and n-hexane in a volume ratio of 1:1. The reaction conditions are the same as for the sulfur resistance test.

2.3. Characterization of catalysts

The acidity of catalysts was measured using in situ IR spectroscopy of adsorbed pyridine. The catalyst powder was pressed into pellet (diameter 14 mm, ca. 20 mg), and pretreated in a vacuum at 623 K for 2 h. Background spectra were recorded at 298 K. Pyridine (0.4 mbar) was introduced at 298 K and keep for 30 min. The spectra were recorded after evacuating at various temperatures, i.e. 473, 573, or 623 K. All spectra were recorded on a Brucker IFS113V IR

Table 1
Summary of catalyst preparation and composition (support HY-Al_2O_3)

Catalyst	Precursor of second metal	Pd content (wt.%)	Second metal (wt.%)	M/Pd atomic ratio
Pd	–	0.6	0	0
Pd-Cr	$(NH_4)_2CrO_4$	0.6	0.6	2.0
Pd-W	$(NH_4)_{10}W_{12}O_{41}\cdot11H_2O$	0.6	0.6	0.6
Pd-La	$La(NO_3)_3$	0.6	0.6	0.8
Pd-Mn	$Mn(NO_3)_2$	0.6	0.6	1.9
Pd-Mo	$(NH_4)_2MoO_4$	0.6	0.6	1.1
Pd-Ag	$AgNO_3$	0.6	0.6	1.0
Cr	$(NH_4)_2CrO_4$	0	0.6	–
W	$(NH_4)_{10}W_{12}O_{41}\cdot11H_2O$	0	0.6	–

spectrometer at 298 K. All spectra shown were corrected for background.

Transmission IR spectra of CO adsorbed on the catalysts were recorded with a Nicolet Impact-410 instrument equipped with an IR cell that allows in situ treatments with different gases at temperatures up to 1000 K. The samples were finely ground with an agate mortar, pressed into wafers with a diameter of 15 mm (ca. 30 mg), and then placed into the IR cell. The samples were dried at 773 K in flowing air for 1 h, and then evacuated to 10^{-5} to 10^{-6} mbar for surface cleaning. Before FFTIR measurements, samples were reduced at the same conditions as those of the catalytic tests, except at a H_2 pressure of 1 atm. After the sample was cooled to room temperature in flowing H_2, the cell was evacuated to 10^{-5} to 10^{-6} mbar, and 25 mbar CO was introduced into the cell and maintained for 30 min. The IR cell was evacuated to a pressure of approximately 10^{-2} mbar to remove the gas phase CO, and IR spectra were recorded. The background of support was subtracted from the IR spectra after CO adsorption.

3. Results and discussion

3.1. Wall reaction

Wall reaction was checked using the sulfur-free feed mentioned above, and the catalyst was replaced by the support HY-Al$_2$O$_3$ (30 wt.% Al$_2$O$_3$). The results showed that there was no wall reaction under the reaction conditions studied.

3.2. Hydrogenation activity of catalysts

In this study, the hydrogenation of toluene (diluted by *n*-hexane) was selected as model for aromatic

hydrogenation in an industrial hydrotreating process for several reasons. In the two-stage process, noble metal catalyst is mainly employed to treat hydrotreated LCO and/or SRLGO, etc. in which monoaromatics usually account for more than 85 wt.% of the total aromatic content [27]. Furthermore, boiling point of toluene is low, which makes analysis by in-line gas chromatography easy. Therefore, toluene, which is the most simple alkyl substituted aromatic, can represent aromatics in the industrial feedstock.

The product distribution is presented in Table 2, showing that the main products of toluene hydrogenation on Pd/HY-Al$_2$O$_3$ are methylcyclohexane (MCH) and dimethylcyclopentane (DMCP). There were also small amounts of other alkanes, benzene and xylene. This revealed that the reactions occurring on the palladium catalyst include hydrogenation (or saturation), isomerization, hydrogenolysis (hydrocracking), and even disproportionation at high temperatures.

Although, we will not attempt to present a clear reaction pathway for the reactions occurring on the catalysts, it is necessary to discuss it based on the products and publications. These HY-Al$_2$O$_3$ supported palladium-based catalysts are typical bifunctional catalysts. Bifunctional catalysis refers to the operation of catalysts comprising a combination of acid and hydrogenation/dehydrogenation functions [28–30]. For the catalysts we prepared, the acidity is mainly provided by HY-zeolite, while the hydrogenation/dehydrogenation activity is exerted by palladium. According to the conventional reaction mechanism, the conversion of an alkane on a bifunctional catalyst goes through three steps [28,29]. The alkane is firstly dehydrogenated on metal sites into alkene. The produced alkene molecules are protonated at the Bronsted acid sites yielding alkylcarbenium ions, which desorb

Table 2
Product distribution of toluene hydrogenation[a]

| Catalyst	Composition (wt.%)				Toluene conversion (wt.%)
	Toluene	MCH	DMCP	Others[b]	
HY-Al$_2$O$_3$	57.8	0	0	0	0
Pd/HY-Al$_2$O$_3$	0	25.4	15.1	13.3	100
Cr/HY-Al$_2$O$_3$	57.0	0	0	0	0
W/HY-Al$_2$O$_3$	56.8	0	0	0	0
Ag/HY-Al$_2$O$_3$	56.8	0	0	0	0

[a] Conditions: 533 K; 4.2 MPa; WHSV, 4.0 h^{-1}; H_2/toluene mole ratio, 40.
[b] The other products include benzene, xylenes and alkanes except for DMCP and MCH.

as alkenes from the acid sites after rearrangements and/or scissions. The desorbed alkenes are then hydrogenated on metal sites to yield saturated products.

There are much less literatures on toluene hydrogenation over supported group VIII metal compared with that on benzene hydrogenation. Similar to benzene hydrogenation on supported metal catalysts [28–35], toluene hydrogenation on supported Pd catalysts should be a stepwise reaction, which may be directly hydrogenated to MCH or desorb as methylcyclohexene during hydrogenation. Another possible source of methylcyclohexene may be from dehydrogenation of MCH. According to the reaction mechanism of bifunctional catalysis [28,29], isomerization to DMCP from methylcyclohexene need Bronsted acid sites on the support HY-Al$_2$O$_3$. The reactions would occur through the pathway depicted in Scheme 1.

The results revealed that single chromium and tungsten had no hydrogenation activity under the reaction conditions. However, the conversion of toluene was 100 wt.% on Pd/HY-Al$_2$O$_3$. Because both the pure Pd and Pd-M bimetallic catalysts contain the same amount of Pd (0.6 wt.%), it could be concluded that Pd is the only active metal during toluene hydrogenation, and loaded Pd is active enough to convert all toluene. It is important to know this because the decrease of
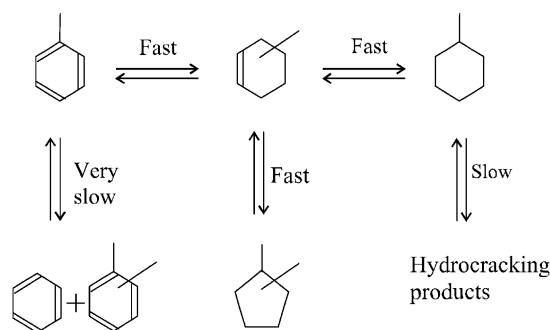
Scheme 1. Reaction network of toluene hydrogenation on Pd/HY-Al$_2$O$_3$. Reaction conditions: 4.2 MPa; 533–573 K; WHSV, 4.0 h^{-1}.

toluene conversion in the sulfur resistance tests could be attributed to poisoning of sulfur in feed.

3.3. Sulfur resistance tests

3.3.1. Effect of the second metal on the activity of the Pd catalysts

Fig. 1 presents the activity of the Pd and Pd-M/HY-Al$_2$O$_3$ (M = Cr, W, La, Mn, Mo, or Ag) catalysts in the hydrogenation of toluene performed under conditions close to realistic industrial conditions
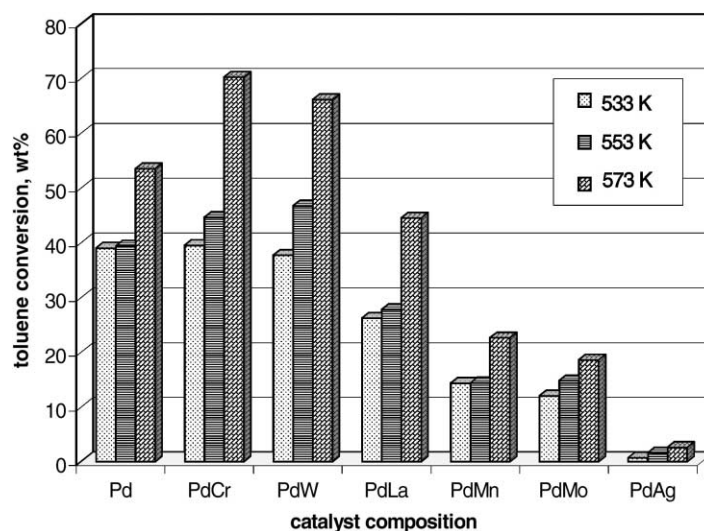

Fig. 1. Toluene conversion on Pd monometallic and bimetallic catalysts. Measured at: 4.2 MPa; WHSV, 4.0 h^{-1}; S, 3000 ppm as thiophene.

($T = 533$–573 K, $P = 4.2$ MPa, WHSV $= 4.0$ h^{-1}, $S = 3000$ ppm in feedstock as thiophene). In order to prevent toluene condensing in the gas line, the H$_2$/toluene ratio is relatively high (H$_2$/toluene mole ratio $= 40$). The reaction usually reached its steady state in 1 h because the sulfur concentration in liquid feedstock was very high. The gas samples were analyzed in-line by gas chromatography after 2 h stabilization. Compared with the results in Table 2, the hydrogenation activity of single Pd catalyst apparently decreased in the presence of sulfur in feed. This indicated that the Pd-based catalysts are sensitive to sulfur compounds, or liable to be poisoned by sulfur.

As mentioned above, both Pd and Pd-M supported catalysts were poisoned by sulfur in the feed. However, the catalysts exhibited different hydrogenation activities at the same reaction conditions in the presence of sulfur, indicating that the extent of sulfur poisoning of the bimetallic catalysts is different from pure Pd. Since the conversion of toluene on Pd/HY-Al$_2$O$_3$ catalyst is 100 wt.% in the absence of sulfur, the conversion of toluene represents sulfur resistance of the catalysts. Of the catalysts tested, although, the second metals were only 0.6 wt.% of the catalysts, the bimetallic Pd-M catalysts exhibited remarkable different activities compared with Pd monometal. La, Mn, Mo, Ag lowered the sulfur resistance of Pd catalysts. Compared with Pd monometallic catalyst, toluene hydrogenation over supported Pd-Mn and Pd-Mo at 553 K was suppressed

from 39.4 to about 14.5 wt.%, by a factor of 2.7. It is surprising that toluene hydrogenation over supported Pd-Ag at 553 K was suppressed to 1.6 wt.%, by a factor of 25 compared with pure Pd. In contrast, Cr and W enhanced the sulfur resistance of Pd catalysts, especially at 553 and 573 K. Compared with single Pd catalyst, toluene hydrogenation activity over supported Pd-Cr at 573 K was enhanced from 53.5 to 70.2 wt.%.

These findings make some sense on research and development of industrial catalysts for deep aromatic hydrogenation of diesel fuel, because alloying metals such as chromium and tungsten are not as expensive as platinum and the amount of the second metal is low.

3.3.2. Effects of the second metal on non-destructive reactions

Figs. 2 and 3 present the selectivity for MCH and DMCP, respectively. Compared with the drastic change of toluene conversion over various Pd-M catalysts, the selectivity for MCH and DMCP remains nearly constant. The reactions to form MCH and DMCP do not change the carbon number of the toluene, and thus, they are called non-destructive reactions.

Apart from the activity itself, the performance of catalysts during the reaction also provides an access to the property of the catalyst surface. From the selectivity for DMCP on Pd and Pd-M bimetallic catalyst, we could obtain some information about the acidity of
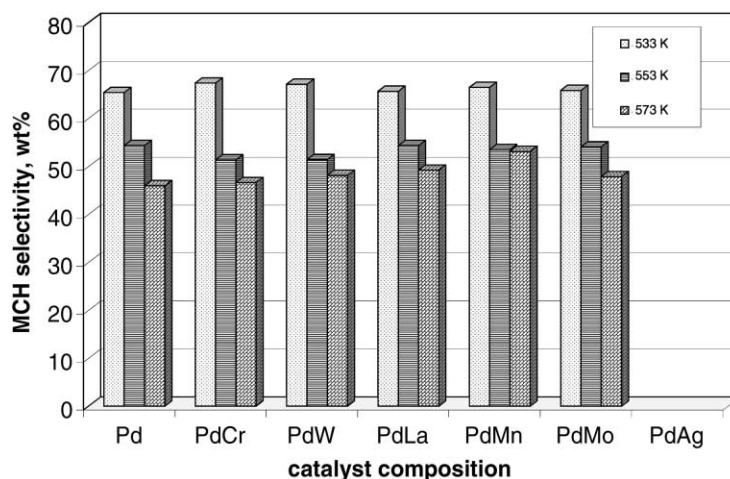

Fig. 2. Methylcyclohexane (MCH) selectivity for toluene hydrogenation on Pd monometallic and bimetallic catalysts. Measured at: 4.2 MPa; WHSV, 4.0 h^{-1}; S, 3000 ppm as thiophene.
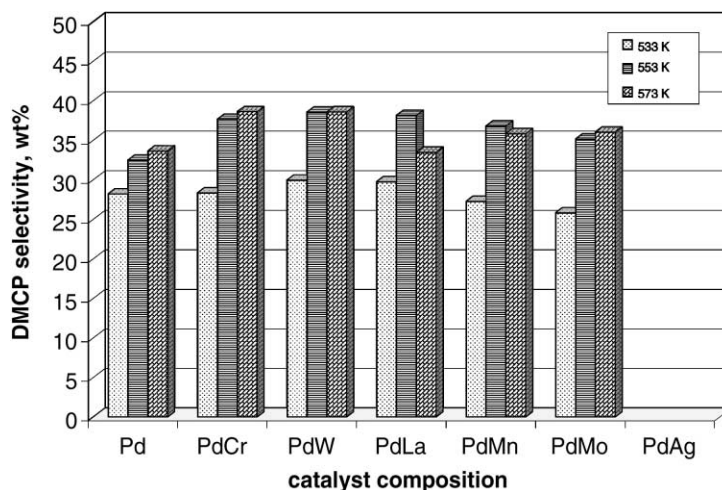
Fig. 3. Dimethylcyclopentane (DMCP) selectivity for toluene hydrogenation on Pd monometallic and bimetallic catalysts. Measured at: 4.2 MPa; WHSV, $4.0\,h^{-1}$; S, 3000 ppm as thiophene.

the catalyst caused from the second metal. The results shown in Figs. 2 and 3 indicate that the selectivity of DMCP and MCH over Pd-M bimetallic catalysts have almost no difference from the single Pd catalyst. It can be concluded from the product distributions that the second metal should have no significant effect on the acidic properties of the catalysts.

3.3.3. Effect of the second metal on destructive reactions

Fig. 4 presents the selectivity for cracking products of palladium based catalysts. The cracking selectivity over the Pd-Ag bimetallic catalyst is not available here because toluene conversion is nearly zero. The cracking products refer to the sum of benzene, xylenes and alkanes except for DMCP and MCH. The reactions
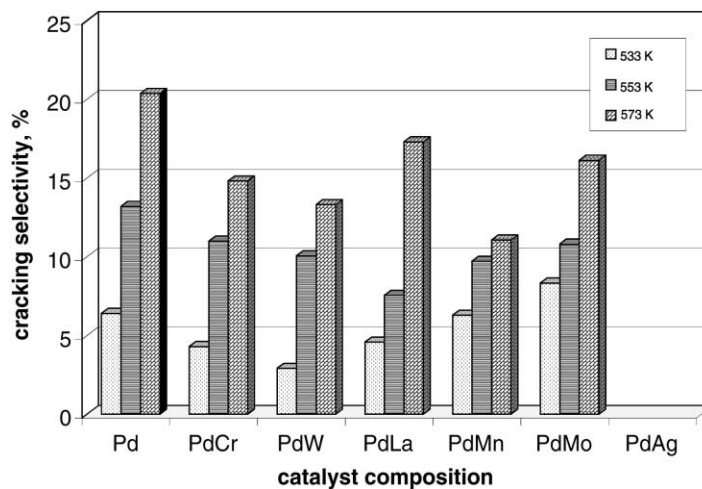

Fig. 4. Cracking selectivity on Pd monometallic and bimetallic catalysts. Measured at: 4.2 MPa; WHSV, $4.0\,h^{-1}$; S, 3000 ppm as thiophene.

to producing these compounds are non-destructive because they involve C–C bond fission. The cracking product selectivity is calculated from the following equation.

$$\text{Cracking selectivity (wt.\%)}$$
$$= \frac{\text{cracking products}}{\text{all the products}} \times 100\%$$

From the results in Fig. 4, the effect of the second metal on the cracking selectivity is much smaller than that on toluene conversion. However, it is worth noting that all the bimetals slightly decrease the cracking product selectivity compared with single Pd. The higher the reaction temperature, the clearer this tendency becomes. Hydrogenolysis of hydrocarbons is an undesirable reaction in the refining process for aromatic hydrogenation of diesel fuel, since it reduces the yield of middle distillate fractions and leads to high hydrogenation consumption. The suppression on hydrogenolysis is, therefore, another advantage of bimetallic Pd catalysts over single Pd.

3.4. Acidic properties of the catalyst

As already known, some metals, especially alkali and alkali earth metals, have a remarkable influence on the acidic properties of the support. In turn, the acidic properties have significant influence on the sulfur resistance of noble metal catalyst. Our previous findings [36] showed that strong Bronsted acidic sites would promote the sulfur resistance of supported Pd catalysts, while Lewis acidic sites do not. From the catalytic performance, it seemed that the acidic properties of the bimetallic catalysts were similar to pure Pd. However, it is still necessary to investigate the acidity before further explanations for the remarkable difference in sulfur resistance between the bimetallic and single Pd catalysts.

IR spectroscopy is a technique which has been very successfully employed to study the acidic properties of heterogeneous catalysts, particularly it can provide information about the types of acid sites on a catalyst surface. Table 3 presents the relative amount of Lewis and Bronsted acid sites on the four typical catalysts, Pd, Pd-Ag, Pd-Cr and Pd-W, which were measured by in situ IR spectroscopy of adsorbed pyridine. The results in Table 3 clearly show that the second metal

Table 3
The relative amount of Lewis acid and Bronsted acid sites on the surface of catalysts

Catalyst	Peak area (473 K)[a]		Peak area (573 K)[a]	
	L	B	L	B
Pd/HY-Al$_2$O$_3$	5.3	15.1	5.5	12.3
Pd-Cr/HY-Al$_2$O$_3$	5.2	14.6	5.8	11.9
Pd-W/HY-Al$_2$O$_3$	5.2	14.9	5.4	12.1
Pd-Ag/HY-Al$_2$O$_3$	5.0	14.7	5.4	11.8

[a] The temperature that pyridine desorbed for 30 min in vacuum.

almost does not change the amounts of the two types of acid sites.

This conclusion is consistent with the deduction from the DMCP selectivity. However, the suppression of the second metals on hydrogenolysis reaction cannot be well accounted for by the mechanism of bifunctional catalysis. This is because the mechanism assumes the rearrangements and/or C–C bond scissions occur on the acidic sites and there is no noticeable acidity changes observed for all the Pd-based catalysts.

There are quite a few literatures concerning about alkanes conversion on supported Pt-based catalysts [37], such as Pt-Pb, Pt-Au and Pt-Ag, Pt-Cu, etc. The authors concluded that additions of the second metals inhibit hydrogenolysis, which can be ascribed to small ensembles of surface platinum atoms caused from alloying.

According to Scheme 1, the hydrogenolysis of toluene (partly) goes through MCH. No results have been reported concerning about the hydrogenolysis of MCH. The inhibited effect was observed for hydrogenolysis of methylcyclopentane on concentrated and dispersed supported Pt catalysts by Gault and coworkers [38]. Methylcyclopentane hydrogenolysis is structure-sensitive on Pt, and MCH is an analogue. Therefore, hydrogenolysis of MCH is considered to be a structure-sensitive reaction, and need multicenter metal sites. It would not be difficult to understand that the second metal suppressed the formation of cracking products: the second metals decrease the fraction of Pd ensembles with atoms in the correct geometry for hydrocracking reaction. However, the suppression effect is small probably because the amount of the second metal is small and the surface area of our support is very high. This showed that the second

metals had an influence on the structure of the active metal clusters on the surface. Bimetallic clusters have probably been formed, or the surfaces of Pd particle have been decorated, partially blocked or separated by the added second metal atoms or its oxides.

Undoubtedly, the drastic changes of the sulfur resistance of the Pd bimetallic catalysts cannot be accounted for by changes of acidic properties. In order to understand the sulfur resistance of Pd-M bimetallic catalysts, geometric and electronic effects of the second metal on Pd active sites should be considered.

3.5. Electronic properties of Pd clusters characterized by IR spectroscopy

As mentioned above, the high sulfur resistance of Pt or Pd on an acidic support arises from the electron-deficient metal particles, $M^{\delta+}$, because of the interaction of metal particles with the Bronsted acid sites. Since the second metals such as Cr, W and Ag do not change the acidic properties of Pd/HY-Al$_2$O$_3$, the electronic properties of Pd should be investigated in order to explain the sulfur resistance of the bimetallic catalysts.

The IR spectra of CO adsorbed on the Pd, Pd-Cr, Pd-W, and Pd-Ag catalysts are shown in Fig. 5. Two bands are observed for all the catalysts at about 1900 and $2100 \, cm^{-1}$, which are respectively assigned to adsorbed CO at bridge adsorption sites and linear sites [39]. Bridge-adsorbed CO prevails on Pd single crystals and concentrated supported Pd catalysts [39–41]. However, the linear CO bands of single Pd prevail probably due to the high dispersion of Pd on the support.

The bands at $2100 \, cm^{-1}$ are more steep, which frequencies are presented. The peak position adsorbed on bimetallic catalyst clusters is different from that on single Pd catalyst. The bands of linear CO on Pd-Cr and Pd-W are located at 2104.22 and $2101.63 \, cm^{-1}$, which are higher than $2096.87 \, cm^{-1}$ of single Pd. However, the band of linear CO on Pd-Ag is located at $2070.37 \, cm^{-1}$, which deviates $26.5 \, cm^{-1}$ from the peak of single Pd to lower frequency.

As to the frequency shift, Sachtler and coworkers [40,41] studied the IR spectra of adsorbed CO on Pd-Ag/SiO$_2$ in detail. They found that CO molecules mainly adsorb on bridge sites of single Pd, and the addition of Ag strongly favored the formation of linear
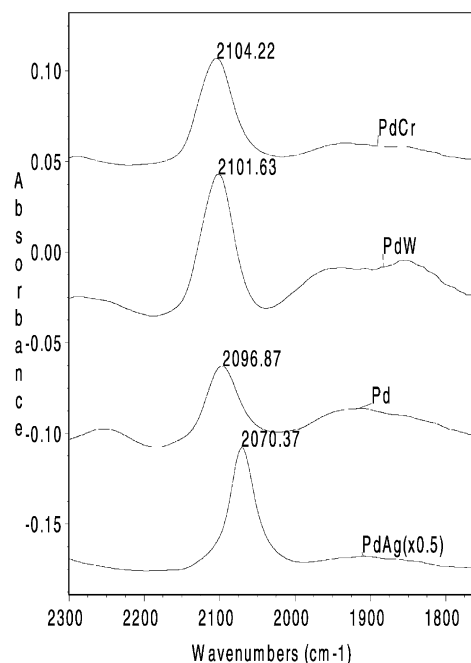

Fig. 5. Infrared spectra of CO adsorbed on Pd, Pd-Cr, Pd-W, and Pd-Ag/HY-Al$_2$O$_3$.

CO due to geometric effect of alloying. According to the backbonding model, the higher the electron density of Pd is, the more C–O bond is weakened, the lower the C–O stretching frequency is. Primet et al. [41] studied the IR spectroscopy of adsorbed CO on Pd-Ag/Al$_2$O$_3$, the frequency shifts (blue shift) of linear CO were partly ascribed to the increase of Pd electron density due to the charge transfer between Pd and Ag. Pd-Cr supported on silica was studied by Renouprez and coworkers [42], a modification of the electronic structure of palladium was found, and also proved by IR spectra of adsorbed CO [43]. The frequency shift of CO absorption bands would confirm that the electron density of Pd is decreased by Cr and W (or their oxides), but increased by Ag.

Since the acidity of the bimetallic catalysts are the same as single Pd, the change of the electronic properties of Pd atoms (or clusters) confirmed the strong interaction and charge transfer between Pd and the second metals or their oxides. Correlated with the catalytic performance, it is clear that the result of interaction determined the sulfur resistance of bimetallic

Pd catalysts. For Pd-Cr and Pd-W interaction, Cr and W decrease the electron density of Pd and enhanced "electron-deficiency" of Pd, the sulfur resistance of Pd have been improved. In contrast, Ag increased the electron density of Pd so that Pd-Ag catalyst was more sensitive to sulfur and exhibited more poor activity.

4. Conclusions

In the presence of 3000 ppm sulfur (as thiophene), toluene hydrogenation was investigated under conditions close to realistic industrial conditions over Pd and Pd-M bimetals on a mixed HY-Al$_2$O$_3$ support. The performance of Pd catalysts was strongly modified by the presence of a second transition metal element such as Cr, W, La, Mn, Mo, Ag. Pd-Cr and Pd-W exhibited higher activity than pure Pd, while the other bimetallic catalysts are less active than single Pd. Pd-Ag bimetallic catalyst was almost completely poisoned. All of the bimetallic catalysts showed nearly the same selectivity for hydrogenation and isomerization products as monometallic Pd catalysts, but slightly suppressed the hydrogenolysis of toluene. The four catalysts, Pd-Cr, Pd-W, Pd-Ag and Pd were characterized by IR spectroscopy. The acidic properties of the catalysts are similar, and thus, the difference in catalytic performance were not caused by change of acidity. CO adsorption IR revealed strong interaction between Pd and the second metal (Cr, W, Ag, etc.). It is concluded that electronic property of Pd is probably responsible for the drastic change in the hydrogenation activity in the presence of sulfur. Alloying with non-noble metal elements is a promising method to improve the sulfur resistance of the noble metal catalysts for aromatic hydrogenation in diesel fuel.

In a future publication, a series of Pd-Cr bimetallic catalysts with various Cr/Pd atomic ratio will be studied in order to further investigate the strong promoting effect of chromium on the sulfur resistance of palladium catalysts [44].

Acknowledgements

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