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**ARTICLE TYPE** 

## Tailoring Supported Palladium Sulfides Catalysts through H<sub>2</sub>-Assisted Sulfidation with H<sub>2</sub>S

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Supported palladium sulfides catalysts are of great interest in selective hydrogenation reactions. In this work, "Pd<sub>4</sub>S", "Pd<sub>3</sub>S", "Pd<sub>16</sub>S<sub>7</sub>" and "PdS" supported on activated carbon were selectively synthesized by tailoring the H<sub>2</sub>-assisted sulfidation of Pd/C with H<sub>2</sub>S at 150-750 °C, and were characterized by means of XRD, XPS, TEM, HRTEM, EDS, BET and H<sub>2</sub>-TPR techniques. The results indicated that sulfidation atmosphere, <sup>10</sup> sulfidation temperature and the metal-support interaction all played important roles in determining the crystal structure and composition of the Pd<sub>x</sub>S<sub>y</sub>/C catalysts, which in turn gave different catalytic performances in the synthesis of N-(1, 3-dimethylbutyl)-N'-phenyl-*p*-phenylenedianine (6PPD) by the reductive N-alkylation of aromatic amines. PdS/C showed the highest selectivity (>97%) and stability among all the Pd<sub>x</sub>S<sub>y</sub>/C catalysts.

#### 1. Introduction

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- <sup>15</sup> Transitional metal sulfides used for catalysts and in materials have been found to be very important for a variety of applications due to their special physical-chemical properties.<sup>1-6</sup> For example, Ni-Mo-S, Co-Mo-S and RuS<sub>2</sub> have been used as catalysts for hydrodesulfidation and hydrodenitrogenation reactions.<sup>1, 2</sup> PtS
- <sup>20</sup> and Rh<sub>2</sub>S<sub>3</sub> have been used for the selective hydrogenation and the sulfur-resistant hydrogenation of organic compounds.<sup>3, 4</sup> Pd sulfides have been proven to be more promising catalysts than other transitional metal sulfides for thiophene hydrogenation and the reductive N-alkylation of aromatic amines due to their ease of <sup>25</sup> formation of active sites and have thereofore attracted increasing
- attention recently. <sup>5-7</sup>

According to the phase diagram of Pd-S, there are five types of Pd-S crystalline phases, namely Pd<sub>4</sub>S, Pd<sub>3</sub>S, Pd<sub>16</sub>S<sub>7</sub>, PdS and PdS<sub>2</sub>.<sup>8</sup> Unsupported palladium sulfides can be generally <sup>30</sup> synthesized by introducing sulfur-containing compounds (CS<sub>2</sub>, H<sub>2</sub>S, or Na<sub>2</sub>S) into an aqueous palladium salt solution, applying the chemical vapor deposition (CVD) method, and by the thermolysis of organometallic compounds.<sup>8-12</sup> Their applications have been found in fabricating photographic and lithographic <sup>35</sup> films, electrolytic deposition of Cu and hydrogen generation.<sup>6, 8, 9</sup>

However, the use of unsupported palladium sulfides used as heterogeneous catalysts in the transformation of organic compounds is scarcely reported because of their lower catalytic activity and stability compared to supported palladium sulfides 40 catalysts.<sup>13, 14</sup>

Supported palladium sulfides are generally prepared through the sulfidation of supported metallic palladium (or oxide) precursors with  $H_2S$  or  $Na_2S$ .<sup>14-23</sup> However, the sulfidation

usually leads to supported palladium sulfides with a structure of <sup>45</sup> amorphous or mixed crystal phases.<sup>7, 17-21</sup> The preparation of supported pallaidum sulfides with a single crystal structure seems to be a great challenge.<sup>24</sup> Up to now, only two papers have reported the synthesis of supported palladium sulfides with single crystal structure: 1) the formation of Pd<sub>16</sub>S<sub>7</sub>/Al<sub>2</sub>O<sub>3</sub>-MoO<sub>x</sub> through

<sup>50</sup> the reaction of Pd/Al<sub>2</sub>O<sub>3</sub>-MoO<sub>x</sub> with H<sub>2</sub>S/H<sub>2</sub> at 400 °C;<sup>22</sup> 2) the formation of Pd<sub>4</sub>S/C by the sulfidation of Pd/C with an aqueous Na<sub>2</sub>S solution in the presence of H<sub>2</sub> at 200 °C;<sup>23</sup> However, the factors that determine the final crystal structure of supported palladium sulfides have not been investigated. There are also no <sup>55</sup> known correlations between the crystal structures of palladium sulfides with their corresponding catalytic performances in chemical reactions. Therefore, it seems necessary to develop methods to synthesize a series of supported palladium sulfides with single crystal structures, so that structure-property <sup>60</sup> relationships can be established.

Synthesis of N-(1,3-dimethylbutyl)-N'-phenyl-pphenylenedianine (6PPD) by reductive N-alkylation of aromatic amines is of importance to caoutchouc and synthetic rubber industries. This reaction starts with a condensation reaction 65 between 4-aminodiphenylamine (ADA) and 4-methyl-2pentanone (MIBK) to form a Ketimine compound (Shiff base), followed by hydrogenation to 6PPD in the presence of noble metal catalysts.<sup>25</sup> But the concomitant undesired reductions, such as the hydrogenolysis reaction of C-N and C=N bonds, and the 70 hydrogenations of carbonyl group and benzene ring are more serious over supported noble metal catalysts due to their high activity.<sup>26</sup> It has been reported that the introduction of sulfur could modify the electronic structure of noble metal catalysts, which minimize the undesired reductions in the selective 75 hydrogenation. 4, 19, 20

In this work, a series of activated carbon supported palladium sulfides catalysts were prepared in which all catalysts had only one crystal structure, being either of "Pd<sub>4</sub>S", "Pd<sub>3</sub>S", "Pd<sub>16</sub>S<sub>7</sub>" or "PdS". The catalysts were created through the H<sub>2</sub>-assisted <sup>5</sup> sulfidation of Pd/C precursors with H<sub>2</sub>S at various temperatures. The effects of the sulfidation temperature, the composition of sulfidation atmosphere and the metal-support interaction on the formation of Pd-S crystalline phases were investigated. The catalytic performances of these as-prepared Pd<sub>x</sub>S<sub>y</sub>/C catalysts in

<sup>10</sup> the synthesis of 6PPD that was used as a model reaction were evaluated, and the structure-property relationships were also investigated.

#### 2. Experimental

#### 2.1 Catalyst preparation

Pd/C catalysts with a nominal Pd loading of 10.0 wt% were prepared by the conventional impregnation method.<sup>27</sup> Prior to impregnation, a commercial activated carbon (China National Medicines Corporation Ltd.) was pretreated with 2.5% HNO3 at 80 °C for 6 h, followed by washing with distilled water until the <sup>20</sup> pH was 7 and then outgassing in a vacuum at 120 °C overnight. After the pretreatment, the impurities of the activated carbon can be removed, which increased structural parameters, such as  $S_{BET}$ , V<sub>micro</sub>, V<sub>total</sub>, and D. It was also beneficial to create an appropriate density of the total acidity on the activated carbon for the <sup>25</sup> preparation of Pd/C catalysts.<sup>27</sup> Three ml of H<sub>2</sub>PdCl<sub>4</sub> (Hangzhou Kaida Metal Catalyst & Compounds Co. Ltd.) aqueous solution (0.05 g/mL) was then added dropwise into 100 ml of aqueous suspension containing 1.5 g of pretreated activated carbon, and then the pH of the solution was adjusted to 10 by the addition of 30 NaOH aqueous solution. This was followed by washing with distilled water until the pH of filtrate was 7 and no chlorine could be observed in filtrate by AgNO<sub>3</sub> titration method. The sample was subsequently reduced with hydrazine hydrate at room temperature and was dried at 110 °C for 7 h. For comparison 35 purposes, a 10.0 wt% Pd/Al<sub>2</sub>O<sub>3</sub> sample was also prepared. This was accomplished by impregnating 1.5g of 20-80 mesh  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Shandong Alumina Factory) with 3 mL of H<sub>2</sub>PdCl<sub>4</sub> aqueous solution (0.05 g·mL<sup>-1</sup>) overnight, followed by drying at 120 °C for 3 h and calcination in air at 500 °C for 4 h. This sample was <sup>40</sup> then reduced in H<sub>2</sub> at a flow rate of 30 mL·min<sup>-1</sup> at 400 °C for 5 h. Unsupported palladium particles were prepared by the direct reduction of 200-400 mesh palladium chloride (PdCl<sub>2</sub>) particles

reduction of 200-400 mesh palladium chloride (PdCl<sub>2</sub>) particle in H<sub>2</sub> at a flow rate of 30 mL min<sup>-1</sup> at 80 °C for 2 h.

The sulfidation of catalysts was carried out by placing 1.5g of <sup>45</sup> sample into an isothermal region of a silica tube (D=20 mm) and heating it to the desired temperature (30-950 °C) at a rate of 10 °C·min<sup>-1</sup> in an N<sub>2</sub> stream (30 mL·min<sup>-1</sup>). Subsequently, the sulfidation was initiated by switching the N<sub>2</sub> stream to a mixed stream of 10%-H<sub>2</sub>S/H<sub>2</sub>(Ar) at the same flow rate and lasted for <sup>50</sup> 3.5 h. Finally, the sample was cooled down to room temperature in an N<sub>2</sub> stream at a flow rate of 30 mL·min<sup>-1</sup>.

#### 2.2 Catalyst Characterization

The samples were characterized using X-ray powder diffraction (XRD), transmission electron microscopy (TEM), <sup>55</sup> energy-dispersive X-ray spectroscopy (EDS), N<sub>2</sub> physisorption, X-ray photoelectron spectroscopy (XPS) and H<sub>2</sub> temperatureprogrammed reduction ( $H_2$ -TPR). The details of these characterization methods can be found in the supplementary material.

#### 60 2.3 Catalytic performance test (Hydrogenation reaction)

The catalytic reaction was performed in a 75 mL stainless steel autoclave reactor (Weihai Automatically-controlled Reaction Kettle Co. Ltd.), in which 0.05g of catalyst, 3.68g of 4aminodiphenylamine (AR/99.7%, Shandong Shengao Chemical

<sup>65</sup> Co. Ltd.) and 10 mL of 4-methyl-2-pentanone (AR/99.5%, Quzhou Juhua Reagents Co. Ltd.) were placed. The reactor was then pressurized with H<sub>2</sub> to the desired pressure (1-4 MPa) after being heated up to 80-200 °C. The beginning of the reaction was indicated by the start of high speed stirring (1200 r/min). The 70 reaction products were analyzed by gas chromatography

(Shimadzu GC-2014) equipped with an FID detector and a capillary column HP-5 ( $\varphi$ 0.320 mm × 30 m).

#### 3. Results and discussion

#### 3.1 Catalyst preparation and characterization

The evolution of the crystal structure of Pd/C in the sulfidation with H<sub>2</sub>S/H<sub>2</sub> in the temperature range of 30-950 °C is presented in the supplementary material (Fig. S1-5). Here Fig. 1 shows the XRD patterns of Pd/C sulfided by H<sub>2</sub>S/H<sub>2</sub> at 150 °C (or 550 °C), 250 °C and 750 °C, which gave rise to the formation of Pd₄S/C, <sup>80</sup> Pd<sub>3</sub>S/C and Pd<sub>16</sub>S<sub>7</sub>/C, respectively. When fresh Pd/C catalyst was sulfided at 150 °C, only a poorly crystallized "Pd<sub>4</sub>S" phase was observed (Fig. 1b). This "Pd4S" phase diminished at the sulfidation temperature of 250 °C and "Pd<sub>3</sub>S" became the only existing phase (Fig. 1d). When the temperature was increased to 85 550 °C (Fig. 1c), the "Pd<sub>4</sub>S" phase reappeared at the expense of the "Pd<sub>3</sub>S" phase and a single well crystallized structure was formed. At temperatures above 600 °C, a "Pd<sub>16</sub>S<sub>7</sub>" phase started to develop and reached its maximum at 750 °C, at which neither "Pd<sub>4</sub>S" nor "Pd<sub>3</sub>S" were present (Fig. 1e). Further increasing the 90 sulfidation temperature led to a mixture of "Pd16S7", "Pd4S" and "Pd<sub>3</sub>S" phases. Hence, an appropriate sulfidation temperature can

generate the desired single phase of "Pd<sub>4</sub>S", "Pd<sub>3</sub>S" or "Pd<sub>16</sub>S<sub>7</sub>" supported on activated carbon.

The sulfidation of Pd/C with  $H_2S/Ar$  in the absence of  $H_2$  shows <sup>95</sup> significantly different results as those with  $H_2S/H_2$ . Single phases of "Pd<sub>4</sub>S", "Pd<sub>3</sub>S" and "Pd<sub>16</sub>S<sub>7</sub>" could not be obtained within the sulfidation temperature range of 150-750 °C (Fig. S7). On the contrary, a single "PdS" phase was observed at 300 °C (Fig. 1f). This suggests that the formation of palladium sulfides supported <sup>100</sup> on activated carbon is highly denpendent on the composition of the sulfidation atmosphere and the temperature.

The presence of single  $Pd_xS_y$  phases supported on activated carbon supported catalysts is further evidenced by HRTEM micrographs (Fig. 2) of the lattice structures of palladium <sup>105</sup> sulfides. EDS measurements indicate that the S/Pd atomic ratios are slightly higher than their nominal stoichiometry value (Table 1). It is due to the accumulation of trace amounts of sulfur on the top of the sample surface evidenced by XPS characterization (Table 1).<sup>10</sup> Another possible explanation is that a trace amount <sup>110</sup> of sulfur penetrated into the activated carbon layers during sulfidation, as suggested by XRD results (Fig. 1). The XRD patterns show that the peak of (0 0 2) facet of the activated Published on 20 August 2013. Downloaded by University of Zurich on 21/08/2013 10:07:54

carbon of sulfided samples shifted to a lower angle compared to that of fresh sample at 20 of  $26^{\circ}$ .<sup>28</sup>



<sup>5</sup> Fig. 1 XRD patterns of samples: (a) fresh Pd/C, (b) Pd<sub>4</sub>S/C (formed at 150 °C in H<sub>2</sub>S/H<sub>2</sub>), (c) Pd<sub>4</sub>S/C (sulfided at 550 °C in H<sub>2</sub>S/H<sub>2</sub>), (d) Pd<sub>3</sub>S/C (sulfided at 250 °C in H<sub>2</sub>S/H<sub>2</sub>), (e) Pd<sub>16</sub>S<sub>7</sub>/C (sulfided at 750 °C in H<sub>2</sub>S/H<sub>2</sub>), (f) PdS/C (sulfided at 300 °C in H<sub>2</sub>S/ Ar). JCPDS PDF: 73-1387, Pd<sub>4</sub>S; PDF: 75-2228, Pd<sub>16</sub>S<sub>7</sub>; PDF: 73-1831, Pd<sub>3</sub>S; PDF: 74-1060, PdS.

The mean particle size of the various palladium sulfides calculated by applying the Scherrer formula was about 30-50 nm (Table 1). This is consistent with the TEM analysis (Fig. 2), which shows the palladium sulfides particles having a size of 5-15 70 nm distributed on activated carbon surface. These results indicate an increase in the average particle size after sulfidation, since the lattice constant of palladium sulfides is much larger than that of pure Pd.<sup>29</sup> Meanwhile, the adsorption of H<sub>2</sub>S decreased the metal–support interaction, making the migration and growth of <sup>20</sup> palladium sulfides particles easier at high sulfidation temperature.<sup>30</sup> Additionally, except for Pd<sub>4</sub>S/C obtained at 150 °C, no significant difference in the S<sub>BET</sub> values and the pore diameter were measured (Table 1), indicating that activated carbon was stable during the sufidation process.

25 Table 1 Summary of characterization results of activated carbon supported palladium sulfides

Catalyst	S/Pd atomic ratio		Particle	SBET	Pore diameter
	EDS	XPS	size/nm <sup>a</sup>	$/m^2.g^{-1}$	/nm
Pd/C	0	0	29.7	1563	3.19
Pd <sub>4</sub> S/C(150 °C)	0.25~0.37	1.02	32.1	1268	3.79
Pd <sub>3</sub> S/C	0.33~0.42	0.59	35.5	1598	3.17
Pd <sub>4</sub> S/C(550 °C)	0.25~0.33	0.49	44.7	1551	3.16
Pd16S7/C	0.44~0.51	0.56	48.6	1407	3.17
PdS/C	1~1.14	1.12	33.6	1473	3.26
<sup>a</sup> : Determined by	XRD.				

In summary, a series of activated carbon supported palladium sulfides catalysts with single crystal structures can be prepared by <sup>30</sup> tuning the sulfidation conditions. To better undertand the formation mechanism of these palladium sulfides, we have investigated the factors that affect the final composition of  $Pd_xS_{yy}$  such as sulfidation atmosphere, temperature and metal-support interaction.



**Fig. 2** HRTEM images of the lattice structure and TEM images of the particle size distribution of (a)  $Pd_4S/C$  (sulfided at 150 °C in  $H_2S/H_2$ ), (b)  $Pd_3S/C$  (sulfided at 250 °C in  $H_2S/H_2$ ), (c)  $Pd_4S/C$  (sulfided at 550 °C in  $H_2S/H_2$ ), (d)  $Pd_1eS_7/C$  (sulfided at 750 °C in  $H_2S/H_2$ ), (e) PdS/C (sulfided at 300 °C in  $H_2S/A_2$ ).

#### 3.2 The effect of sulfidation atmosphere and temperature

The "Pd<sub>4</sub>S", "Pd<sub>3</sub>S" and "Pd<sub>16</sub>S<sub>7</sub>" could be sequentially formed with the increase in sulfidation temperatures using  $H_2$  as the balance gas. According to the phase diagram, it was difficult to

obtain single "Pd<sub>4</sub>S" and "Pd<sub>3</sub>S" phases through the reaction Pd metal and sulfur powder under vacuum.<sup>8</sup> For example, single "Pd<sub>4</sub>S" phase could not be obtained at temperatures below 767 °C under vacuum, because a mixed phase of "Pd<sub>3</sub>S" and "Pd<sub>4</sub>S" 5 could be formed when the atomic percent of sulfur is above 20%.<sup>8</sup> Furthermore, according to the values of  $\Delta G$  for the formation of different phases of palladium sulfides, the formation rate follows the order: "PdS"> "Pd<sub>16</sub>S7"> "Pd<sub>3</sub>S"> "Pd<sub>4</sub>S". And it has been reported that "Pd16S7" is an intermediate of "PdS" in the 10 direct sulfidation of Pd with sulfur powder.<sup>31</sup> But our studies showed that when using H<sub>2</sub> as the balance gas, the "PdS" phase could not be formed by the further sulfidation of "Pd<sub>16</sub>S<sub>7</sub>" with H<sub>2</sub>S even after prolonged sulfidation time (8 h) or at higher temperature (800-950 °C) (Fig. S5-6). In contrast, when using Ar 15 as the balance gas, the final composition of  $Pd_xS_y$  were significantly different from the results obtained using H<sub>2</sub> as balance gas, and the single "PdS" phase could be formed at a sulfidation temperature of 300 °C. Therefore, the formation of single phase is highly dependent on the sulfidation atmosphere.



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Fig. 3 XPS analysis of Pd/C treated with H<sub>2</sub>S/Ar at 30  $^\circ\text{C}$  for 3.5 h

XPS spectra (Fig. 3) shows that there were three forms of sulfur species with peaks, including 162.1 eV ( $S^{2-}$ ), 164.1 eV ( $S_{n}$ ) 25 and 168.0 eV (S<sup>6+</sup>) for the sulfided Pd/C formed at 30 °C in a flow of H<sub>2</sub>S/Ar.<sup>32</sup> These findings indicate that H<sub>2</sub> and chemisorbed sulfur species could easily be produced via the dissociation of HS and H<sub>2</sub>S at low temperatures. Therefore, sulfidation under both  $\mathrm{H_2S/H_2}$  and  $\mathrm{H_2S/Ar}$  can be considered as 30 H2-assisted sulfidation. Hensen reported that the presence of different Pd sulfide phases is mainly dependent on the H<sub>2</sub>S/H<sub>2</sub> ratio.<sup>16</sup> They observed Pd metal was formed at a H<sub>2</sub>S/H<sub>2</sub> ratio below 0.008, Pd<sub>4</sub>S was formed at H<sub>2</sub>S/H<sub>2</sub> ratios between 0.008 and 0.025, and PdS at higher ratios.<sup>16</sup> Therefore, the formation of 35 the "PdS" phase using Ar as the balance gas can be attributed to the higher H<sub>2</sub>S/H<sub>2</sub> ratio in the sulfidation atmosphere than that required for the formation of "PdS<sub>1-x</sub>" ( $0 \le x \le 1$ ) that is normally formed using  $H_2$  as the balances gas.

Meanwhile, mixed Pd–S phases were obtained at 550  $^{\circ}$ C and 40 750  $^{\circ}$ C using Ar as the balance gas, indicating that the

dissociation rate of H<sub>2</sub>S was influenced by the sulfidation temperature.<sup>16</sup> In addition, a high sulfidation temperature may improve the degree of lattice perfection, resulting in the formation of well-crystallized phase. For example, "Pd<sub>4</sub>S" could <sup>45</sup> be formed at 150 °C and 550 °C in the presence of H<sub>2</sub>S/H<sub>2</sub>. Diffraction peaks of "Pd<sub>4</sub>S" formed at 550 °C showed higher intensity than those of "Pd<sub>4</sub>S" formed at 150 °C, indicating that "Pd<sub>4</sub>S" formed at 150 °C was poorly crystallized and its lattice may have imperfections, such as dislocations and vacancies.<sup>31</sup> Note that the broadening appearance of diffraction profile of Pd<sub>4</sub>S/C(150°C) could be attributed to the fact that this sample contains polycrystalline agglomerates carried out during the sulfidation process.<sup>33</sup>

Therefore, the sulfidation atmosphere and temperature played <sup>55</sup> a crucial role in the shift of phase equilibrium, which tailored the formation of single "Pd<sub>4</sub>S", "Pd<sub>3</sub>S", "Pd<sub>16</sub>S<sub>7</sub>" or "PdS" phase. But it should be noted that the formation of "PdS<sub>2</sub>" that was supposed to form according to the phase diagram, was not observed in our study, indicating that "PdS<sub>2</sub>" may only be formed through the <sup>60</sup> reaction of Pd metal and sulfur powder.<sup>8, 34</sup>



Fig. 4 H<sub>2</sub>-TPR analysis of samples: (a) Carbon (sulfided at 30  $^{\circ}$ C in H<sub>2</sub>S/H<sub>2</sub>); (b) Pd-PdS<sub>x</sub>/C (sulfided at 30  $^{\circ}$ C in H<sub>2</sub>S/H<sub>2</sub>); (c) Carbon <sup>65</sup> (sulfided at 150  $^{\circ}$ C in H<sub>2</sub>S/H<sub>2</sub>); (d) Pd<sub>4</sub>S/C (sulfided at 150  $^{\circ}$ C in H<sub>2</sub>S/H<sub>2</sub>); (e) Pd<sub>3</sub>S/C (sulfided at 250  $^{\circ}$ C in H<sub>2</sub>S/H<sub>2</sub>); (f) PdS/C(sulfided at 300  $^{\circ}$ C in H<sub>2</sub>S/Ar); (g) Pd<sub>4</sub>S/C (sulfided at 550  $^{\circ}$ C in H<sub>2</sub>S/H<sub>2</sub>); (h) Pd<sub>16</sub>S<sub>7</sub>/C (sulfided at 750  $^{\circ}$ C in H<sub>2</sub>S/H<sub>2</sub>).

In order to further understand the effect of sulfidation atmosphere and temperature on the formation of palladium sulfides, the Pd-S bond strength of Pd<sub>x</sub>S<sub>y</sub>/C was analyzed by H<sub>2</sub>-TPR as shown in Fig. 4. Since there is no desorption of H<sub>2</sub>S over the activated carbon sulfided at 30 °C (Fig. 4a), the peak at 327 °C
<sup>75</sup> observed over the Pd-PdS<sub>x</sub>/C sulfided at 30 °C can be assigned to chemisorbed S species on the Pd surface (Fig. 4b).<sup>35</sup> A broad peak located at 434 °C can be seen over the activated carbon sulfided at 150 °C (Fig. 4c), which was ascribed to the reduction of sulfur in the layers of the activated carbon support, as
<sup>80</sup> evidenced by XRD (Fig. 1).<sup>28</sup> According to the hydrogen consumption during H<sub>2</sub>-TPR experiments (Fig. S8 and Table S1),

the peak at 379 °C is referred to the reduction of "Pd<sub>4</sub>S" formed at

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150 °C (Fig. 4d). The reduction peak of "Pd<sub>3</sub>S" formed at 250 °C should be composed of multiple peaks with a maximum at 338 °C and a shoulder peaks at 380 °C (Fig. 4e). This result indicates that "Pd<sub>3</sub>S" was first reduced into "metal Pd" with a minor 5 amount of "Pd<sub>4</sub>S", and then "Pd<sub>4</sub>S" was reduced to "metal Pd" with the increasing of temperature. In addition, "PdS" showed convoluted reduction peaks offsetting at 289 °C up to 427 °C with a maximum at 393 °C and two shoulder peaks at 343 °C and 384 °C, respectively (Fig. 4f). They correspond to the transition from 10 a part of "PdS" to "Pd-Pd<sub>4</sub>S-PdS" and then "Pd-PdS" at reduction temperature of 343 °C and 384 °C, respectively, which was followed by the direct reduction of the remaining "PdS" to "metal Pd" at 393 °C. It is also found the peak at 379 °C referred to the reduction of "Pd<sub>4</sub>S" formed at 150 °C (Fig. 4d) disappears on the 15 "Pd<sub>4</sub>S" formed at 550 °C (Fig. 4g), and only the peak at 327 °C could be detected. Furthermore, since almost no reduction is observed on Pd<sub>16</sub>S<sub>7</sub>/C (Fig. 4h), this catalyst is assumed to be the most stable among all the studied catalysts in H<sub>2</sub>. Therefore, a high sulfidation temperature is generally associated with a high  $_{20}$  stability of Pd<sub>x</sub>S<sub>y</sub>/C in H<sub>2</sub>. And it is thus concluded that the Pd-S bond strength (stability in H<sub>2</sub>) of palladium sulfides follows the order: "Pd<sub>16</sub>S<sub>7</sub>" (sulfided at 750  $^{\circ}$ C) > "Pd<sub>4</sub>S" (sulfided at 550  $^{\circ}$ C) > "PdS" (sulfided at 300 °C) > "Pd<sub>4</sub>S" (sulfided at 150 °C) >"Pd<sub>3</sub>S" (sulfided at 250 °C) > "Pd-PdS<sub>x</sub>" (sulfided at 30 °C). Since  $_{25}$  all the studied palladium sulfides are stable below 250 °C in H<sub>2</sub>, it is reasonable to suggest that no decomposition of sulfides would occur during the catalytic hydrogenation.

#### 3.3 The effect of metal-support interaction

We have demonstrated that the " $Pd_{16}S_7$ " phase could not be 30 formed over Pd/C until the sulfidation temperature was above 600 °C, whilst an unsupported single "Pd<sub>16</sub>S<sub>7</sub>" phase (Fig. 5a) could be obtained through the reaction of unsupported Pd particles with H<sub>2</sub>S/H<sub>2</sub> at 300 °C. We propose that the formation of  $Pd_xS_y/C$  was influenced by the presence of support. Koki reported 35 that Pd/TiO2 and Pd/Al2O3 sulfided at room temperature displayed a significant difference in sulfur tolerance and Pd-S bond strength. This was mainly due to the different electron densities of the Pd metals influenced by the interaction between the Pd metals and the support.<sup>36</sup> In general, a weak Pd-S bond indicates a low 40 electron density of Pd metals, which is induced by a strong metalsupport interaction, and vice versa. This is due to the fact that a strong metal-support interaction induces the electron transfer from Pd metals to support, the electron density of Pd is thus reduced and the Pd-S bond is weakened.<sup>36</sup> If the metal-support

- $_{45}$  interaction is weak, Pd metals have a high electron density and tend to bond strongly with sulfur. Therefore, the higher sulfidation temperatures required for the formation of Pd\_{16}S\_7/C compared to that of unsupported Pd\_{16}S\_7 particles can be attributed to the metal-support interaction.
- <sup>50</sup> In order to gain an understanding of the effect of the metalsupport interaction, Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/C and unsupported Pd particles sulfided with H<sub>2</sub>S/H<sub>2</sub> at 300 °C were compared. It is found that Pd<sub>4</sub>S/Al<sub>2</sub>O<sub>3</sub>, Pd<sub>4</sub>S-Pd<sub>3</sub>S/C and unsupported Pd<sub>16</sub>S<sub>7</sub> particles were formed after the sulfidation (Fig. 5), which suggests that the
- <sup>55</sup> metal-support interaction indeed affected the formation of palladium sulfides during the sulfidation process. According to the Pd-S bond strengths of palladium sulfides as demonstrated in Section 3.2: "Pd<sub>16</sub>S<sub>7</sub>" > "Pd<sub>4</sub>S" > "Pd<sub>3</sub>S", the catalysts with





Fig. 5 XRD patterns of samples treated with  $H_2S/H_2$  at 300 °C for 3.5 h. (a)  $Pd_{16}S_7$  (b)  $Pd_3S$ - $Pd_4S/C$  (c)  $Pd_4S/Al_2O_3$ 

<sup>65</sup> trend indicates that the interaction between Pd metals and activated carbon is stronger than Al<sub>2</sub>O<sub>3</sub>. This is because the pretreatment of activated carbon with HNO<sub>3</sub> produced a great amount of acidic oxide groups assembling densely on the activated carbon, resulting in a strong interaction between the <sup>70</sup> oxygen-containing groups and the Pd metal precursor.<sup>27</sup> On the contrary, the unsupported Pd particles that gave rise to "Pd<sub>16</sub>S<sub>7</sub>" after sulfidation have the least metal-support interaction (actually no metal-support interaction) among these three catalysts.

#### 3.4 Catalytic performances

The reaction scheme for the synthesis of N-(1, 3dimethylbutyl)-N'-phenyl-p-phenylenedianine (6PPD) is shown in Fig. 6. As shown in Table 2, ADA was completely converted in only 0.4 h, but a lower selectivity (21.7%) was obtained over Pd/C catalyst under the reaction conditions of 200 °C and 4 MPa. 80 The main by-products were N-(1, 3-dimethylbutyl)-N'cyclohexane-p-phenylenedianine, 4-methylpentan-2-ol and 2methylpentane, which were derived from the hydrogenation of 6PPD, MIBK and the hydrogenolysis of ketimine, respectively.<sup>19, 20, 37</sup> In contrast, a higher selectivity ( $\geq$ 94.6%) 85 could be obtained over activated carbon supported palladium sulfides catalysts under the same reaction condition but with a longer reaction time (5-6 h). Furthermore, Fig.7 showed that the binding energies of Pd 3d<sub>5/2</sub> of Pd<sub>x</sub>S<sub>v</sub>/C with different phase structures (Table S2), featured at lower (336-336.8 eV) and 90 higher binding energy (337.2-337.9 eV), are attributed to Pd atoms bonded with  $S_n \& S^{6+}$  and  $S^{2-}$ , respectively.<sup>28, 32</sup> It is worth



**Fig. 6** Reaction scheme for the synthesis of N-(1, 3-dimethylbutyl)-N'phenyl-*p*- phenylenedianine (6PPD)

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to note that the yield of 6PPD over  $Pd_xS_y/C$  with different phase structures was in the order:  $PdS/C > Pd_4S/C(150 °C) >$  $Pd_4S/C(550 \ C) > Pd_3S/C > Pd_{16}S_7/C$ , which was consistent with the order of the binding energy of Pd 3d<sub>5/2</sub> (Fig.7 and Table 5 S2).

It is well known that the adsorption behaviour of substrates, which is highly dependent on the electronic structure of the surface of catalysts, plays an important role in the yield of products.<sup>37</sup> Side-on via  $\sigma$ -donation and  $\pi$ -backdonation (i.e. $\sigma/\pi$ -10 adsorbed imine) are the most possible coordination states for the adsorption of the C=N bond and the C=O bond of ketimine and MIBK, respectively. Then, the activation energies of C=N bond formation and C=O bond cleavage are lowered due to the presence of the favorable coordination states.<sup>38, 39</sup> And the most 15 stable adsorption model for the phenyl group in the vicinity of the C=N bond is a flat-lying state by coordinating the phenyl group to the Pd surface, which also promotes the activation of phenyl ring.<sup>38</sup> The high yield to 6PPD obtained over catalysts can be thus attributed to the relatively low backdonation from electron 20 deficient palladium atoms to the adsorbates, thereby reducing the activation of phenyl ring, C=O bond and C=N bond.

Table 2 Catalytic performances of activated carbon supported palladium sulfides and Pd/C catalysts in the synthesis of 6PPD<sup>a</sup>

Catalyst	T/h	C/%	S/%	
Cumiyst			Ketimine	6PPD
Pd/C <sup>b</sup>	3	99.5	4.1	78.9
Pd/C	0.4	100		21.7
Pd <sub>4</sub> S/C(150 °C)	5	100		96.6
Pd <sub>4</sub> S/C(150 °C) Reused 2	6	98.9	0.2	95.3
Pd <sub>3</sub> S/C	6	98.3	0.5	96.1
Pd <sub>4</sub> S/C(550 °C)	6	97.6	0.6	97.5
Pd <sub>16</sub> S <sub>7</sub> /C	6	91	1.7	96.5
PdS/C	6	100		96.9
PdS/C Reused 2	6	100	0.1	97.1
PdS/C Reused 3	6	99.7	0.2	97.5

<sup>a</sup>: Reaction conditions: 4-aminodiphenylamine (ADA) 3.68 g, 4-methyl-2pentanone (MIBK) 10 mL, catalyst 0.05 g, 200 °C, 4 MPa.

Reaction b was carried out under the reaction conditions of 80 °C and 1 MPa.

In addition, since PdS/C and Pd<sub>4</sub>S/C (150 °C) catalysts showed 30 better catalytic properties, their reusability in this reaction was investigated under the same reaction conditions. ADA could not be completely converted even after longer reaction time (6 h) under the same reaction conditions and the yield of 6PPD was decreased to 94.2% over Pd<sub>4</sub>S/C (150 °C) catalyst. The phase 35 structure of the used Pd<sub>4</sub>S/C (150 °C) catalyst did not change as compared to that of fresh one (Fig. S9), but XPS results (Fig. S10 and Table S3) shows that its lower (higher) binding energy of Pd

- 3d<sub>5/2</sub> and surface S/Pd atomic ratio decreased to 335.9 eV (336.9 eV) and 0.28, respectively. It indicates that the high activity of <sup>40</sup> fresh Pd<sub>4</sub>S/C (150  $\degree$ C) may be attributed to the high sulfur content
- on the catalyst surface compared to that of other  $Pd_xS_y/C$ catalysts, because the surface sulfur atoms could increase the dissociation rate of H<sub>2</sub> on Pd atoms during the hydrogenation.<sup>10</sup> On the other hand, PdS/C could be reused at least for three times
- <sup>45</sup> without any significant loss of catalytic activity and yield (≥97%). Moreover, there was no change in the phase structure (Fig. S9) and the binding energy of Pd  $3d_{5/2}$  between fresh and used PdS/C (Fig. S11 and Table S3). The better catalytic properties of PdS/C catalyst than that of Pd<sub>4</sub>S/C (150  $^{\circ}$ C) can thus be attributed to its 50 more stable surface electronic structure.



**Binding Energy/eV** 

Fig. 7 XPS spectra of Pd<sub>x</sub>S<sub>y</sub>/C with different phase structures: (a) Pd<sub>4</sub>S/C (sulfided at 150 °C in H<sub>2</sub>S/H<sub>2</sub>) (b) Pd<sub>3</sub>S/C (sulfided at 250 °C in H<sub>2</sub>S/H<sub>2</sub>) (c) Pd<sub>4</sub>S/C (sulfided at 550  $^{\circ}$ C in H<sub>2</sub>S/H<sub>2</sub>) (d) Pd<sub>16</sub>S<sub>7</sub>/C (sulfided at 750  $^{\circ}$ C 55 in H<sub>2</sub>S/H<sub>2</sub>) (e) PdS/C (sulfided at 300 °C in H<sub>2</sub>S/ Ar)

#### 4. Conclusions

A H<sub>2</sub>-assisted sulfidation method for the preparation of supported palladium sulfides with single crystal structures was developed. "Pd<sub>4</sub>S", "Pd<sub>3</sub>S" and "Pd<sub>16</sub>S<sub>7</sub>" supported on activated 60 carbons were prepared in H<sub>2</sub> atmosphere at 150  $^{\circ}$ C (or 550  $^{\circ}$ C), 250 °C and 750 °C, respectively. "PdS" supported on activated carbon was formed in Ar atmosphere at 300 °C. The results indicated that sulfidation atmosphere and temperature are the determining factors in the selective formation of palladium 65 sulfides phase supported on activated carbon. Moreover, in the comparison of the sulfidation results of Pd/C, Pd/Al<sub>2</sub>O<sub>3</sub> and unsupported Pd particles, the Pd-S bond strength of palladium sulfides phase was found dependent on the interaction between metal and support. The catalytic performances of Pd<sub>x</sub>S<sub>y</sub>/C 70 catalysts are highly dependent upon their crystalline phase and composition, and PdS/C showed a higher yield and stability than other  $Pd_xS_v/C$  catalysts in the synthesis of 6PPD.

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#### <sup>80</sup> Notes and references

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### Tailoring Supported Palladium Sulfides Catalysts Through H<sub>2</sub>-Assisted Sulfidation with H<sub>2</sub>S

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 $Pd_4S/C$ ,  $Pd_3S/C$ ,  $Pd_{16}S_7/C$  and PdS/C catalysts were selectively prepared and the structure-property relationships were established.