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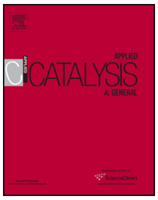

Catalytic hydrogenation of sulfur-containing nitrobenzene over Pd/C catalysts: *In situ* sulfidation of Pd/C for the preparation of Pd_xS_y catalysts

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ABSTRACT

The preparation of supported palladium sulfides catalysts has attracted much attention due to their good sulfur-resistant properties in the hydrogenation of sulfur-containing compounds. In this work, we unambiguously demonstrated that Pd/C catalyst could be *in situ* sulfided by organic sulfur-containing reactant molecules and the sulfidation was highly dependent on temperature. The *in situ* sulfidation of Pd/C catalyst was composed of a reaction of Pd with the sulfur derived from the cleavage of C—S bond of sulfur-containing reactant molecules, followed by a transformation to Pd_xS_y at high temperatures (around 120 °C). The sulfided Pd/C catalyst could be used for at least 18 recycles without a significant loss in its activity during the hydrogenation of sulfur-containing nitrobenzene at 180 °C with 3 MPa H_2, which could be attributed to the stable presence of Pd_4S and $Pd_{16}S_7$.

1. Introduction

Sulfur-containing anilines are important intermediates for the synthesis of medicines including antibiotic, insecticides, fungicides and herbicides [1]. They are generally produced from the reduction of sulfur-containing nitrobenzene using compounds such as NaS_2, N_2H_4, Fe/HCl and Zn/NH_4Cl as nucleophilic reductants [2–5]. However, these reductants are hazardous to environment and make the purification of final products difficultly. Green synthesis based on heterogeneous catalytic hydrogenation of sulfur-containing nitrobenzene is considered to be an attractive route for the preparation of thio-anilines (as shown in reaction 1) [6]. However, the possible inhabitation of H_2 dissociation by the strong chemisorption of sulfur-containing reactants on active sites of the metal catalysts yet remains as a great challenge, which could result in a sharp decline in the catalysts' activities [7].

$$R - S - Ph - NO_2 + 3H_2 \xrightarrow{\text{Catalyst}} R - S - Ph - NH_2 + 3H_2O\ (R = C_nH_{2n+1},\ Ph,\ Ph - S) \quad (1)$$

On the other hand, sulfur-containing compounds may act as catalyst promoter or selectivity modifier in heterogeneous catalysis [8–10]. Moreover, pre-sulfided metal catalysts are well known to be sulfur-resistant and have been extensively employed for hydrodesulfurization (HDS) reactions at 240–360 °C [11,12]. The steady good catalytic properties of pre-sulfided metals are attributed to the stable composition of active phases maintained by the dynamic quasi-equilibrium between the chemical states of the metal sulfides, in which the catalysts were reduced by H_2 into metallics, but immediately re-sulfided again by the sulfur from the HDS of sulfur-containing compounds [13,14]. However, few knowledge could be obtained about the thorough investigation of the hydrogenation of organic sulfur-containing compounds (especially of sulfur-containing nitrobenzene) over metal sulfides catalysts [15–17]. It is probable that the dynamic equilibrium is hardly available at low temperatures at which the liquid hydrogenation is generally operated, which can finally lead to the deactivation of the catalysts during recycling process [15,16]. When the hydrogenation reaction is carried out at higher temperature that is close to the normal HDS reaction temperature, the selectivity of product is poor owing to the C—S bond cleavage or the rapid deactivation of the catalysts due to the coke formation [18,19].

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Supported Pd sulfides are generally recognized as more appropriate catalysts for the hydrogenation of organosulfur because of their higher hydrogenation and lower hydrogenolysis activity of C—S bond than other metal sulfides catalysts [20–23]. However, very limited information is available on the catalytic stability and the active phase of palladium sulfides catalysts for the hydrogenation of organosulfur. Novakova et al. found that high H_2 pressure could inhibit the chemisorption of sulfur on 10-wt% Pd/C catalyst during the hydrogenation/hydrogenolysis of 4,4′-dinitrodiphenyldisulfide to 4-aminothiophenol and the catalyst could be reused for 7 times [15]. Nevertheless, there was still a clear decrease in the reaction rate with the increase of the recycle numbers. They suggested that the decreased activity might be due to the transformation of an active amorphous surface sulfide into an inactive phase (*e.g.* Pd_4S) [15]. But Miller et al. reported that the dissociation rate of H_2 on the Pd_4S surfaces could still reach one third of that of metal Pd at 450 °C even in the presence of H_2S [24,25]. Moreover, supported palladium sulfides catalysts are generally synthesized through pre-sulfidation of supported Pd metal catalysts using H_2S, Na_2S or organic sulfur-containing molecules as vulcanizators, but such method has the problem of high environmental pollution and high industrialization cost [20–28].

Therefore, the aim of our study is to develop a novel “green” method to produce supported palladium sulfides catalyst, and obtain more detailed insight into their stability and active phases. We discovered a key phenomenon known as *in situ* sulfidation that Pd supported on activated carbon could be sulfided by the sulfur from sulfur-containing compounds to form Pd_xS_y (*e.g.* Pd_3S, $Pd_{16}S_7$ and PdS) during the hydrogenation of sulfur-containing nitrobenzene. The stability of the *in situ* sulfided catalyst and the activity of the various active phases of palladium sulfides were investigated through XRD and XPS characterization. Temperature was found to be a dominant factor in the *in situ* sulfidation process. The *in situ* sulfidation can reduce the cost of catalyst preparation by avoiding the pre-sulfidation of metal catalysts using H_2S as vulcanizator, but also render the catalyst a better activity and stability in the hydrogenation of sulfur-containing nitrobenzene, which will be of great significance to future commercial applications.

2. Experiments and methods

2.1. Catalysts preparation and characterization

The sample of 10 wt%-Pd/C catalyst was prepared by the impregnation method [29], and its specific surface area (S_{BET}) was measured to be 1563 $m^2\ g^{-1}$. Prior to the impregnation, a commercial activated carbon (China National Medicines Corporation Ltd.) was pretreated with 2.5% HNO_3 at 80 °C for 6 h. The pretreated carbon was then washed with distilled water until the pH was 7 and outgassed in vacuum at 120 °C overnight. The pretreatment is beneficial to create an appropriate density of total acidity on the activated carbon for the preparation of Pd/C catalysts [29]. A volume of 3 mL H_2PdCl_4 (Hangzhou Kaida Metal Catalyst & Compounds Co. Ltd.) aqueous solution (0.05 g mL^{-1}) was dropped into the suspension of 1.5 g of activated carbon, and the pH value of the solution was regulated to 11 by the addition of NaOH aqueous solution. Eventually, the catalyst was reduced with hydrazine hydrate at room temperature, and dried at 110 °C for 7 h.

Characterization of the catalysts were carried out by powder XRD at room temperature before and after the hydrogenation reaction using an X'Pert PRO diffractometer (PNAlytical Co.) equipped with a Cu $K\alpha$ radiation source operating at 40 kV and 40 mA. XPS measurements were performed on a Thermo ESCALAB 250 Axis Ultra spectrometer using monochromatic Al Kα radiation ($h\nu$ = 1486.6 eV). All binding energy (BE) values were calibrated by using the value of contaminant carbon (C 1s = 284.8 eV) as a reference.

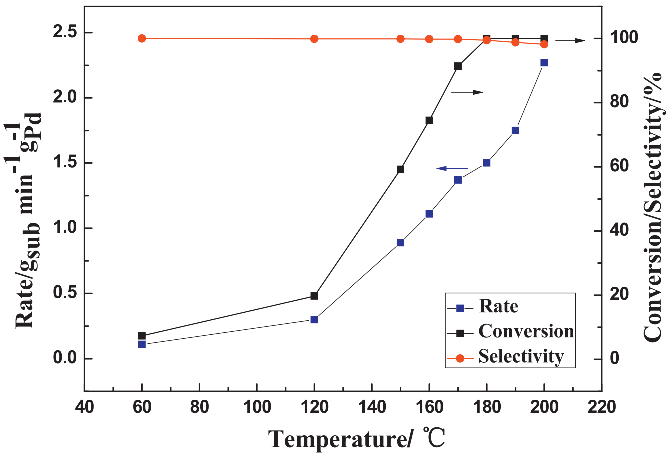


Fig. 1. Hydrogenation of 4-nitrothioanisole on Pd/C catalyst at various temperatures. Reaction conditions: 0.2 g 10 wt.% Pd/C, 20 g substrate, 150 mL toluene, 3 MPa of H_2, and reaction time of 660 min for the temperatures of 60–180 °C, 570 and 440 min for 190 and 200 °C, respectively.

2.2. Hydrogenation tests

0.2 g of Pd/C catalyst, 20 g of 4-nitrothioanisole (AR/99.7%, Hubei Laohekou Chemical Co. Ltd.) and 150 mL of toluene were charged into a 500 mL stainless steel autoclave. The reactor was pressurized with H_2 to 3 MPa after being heated up to the desired reaction temperatures (60–200 °C).

For recycling reactions, 1.0 g of Pd/C catalyst was used for the hydrogenation of 4-nitrothioanisole with a catalyst/substrate weight ratio of 1:20 at 180 °C and 3 MPa. The used catalyst was then filtered, washed with toluene ($3 \times 10\ cm^3$) at room temperature. 0.1 ± 0.01 g of catalyst after each reaction was characterized by XRD, and the residual catalyst was reused in reactions.

In order to study the universality of *in situ* sulfidation in the hydrogenation of sulfur-containing compounds, the hydrogenation reactions of a series of these compounds as listed in Table 1 (AR/98%, Aladdin reagent Co. Ltd.) were performed in a 75 mL stainless steel autoclave reactor under the conditions of 2.0 g substrates, 0.05 g Pd/C, 10 mL toluene, and at 180 °C and H_2 pressure of 3.0 MPa. All reaction products were analyzed by gas chromatography (Shimadzu GC-2014) equipped with FID and a capillary column HP-5 (φ0.320 mm × 30 m).

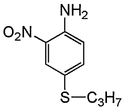
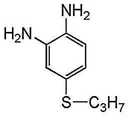
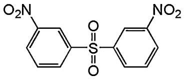
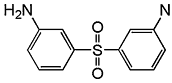
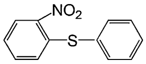
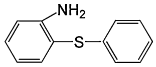
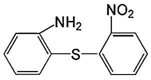
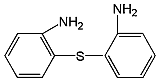
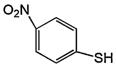
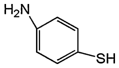
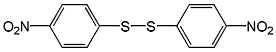
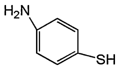
Here, the yield of the desired product was defined as the conversion of the reactant multiplied by the selectivity of the desired product.

3. Results and discussion

3.1. In situ *sulfidation of Pd/C with sulfur-containing reactants*

Fresh Pd/C catalyst was used for the hydrogenation of 4-nitrothioanisole at 60–200 °C and 3 MPa of H_2 pressure, and the experimental results are shown in Fig. 1. The yield of desired product (4-aminothioanisole) and the reaction rate at 60 °C were only 7.4% and 0.11 $g_{sub}\ min^{-1}\ g_{Pd}^{-1}$, respectively. However, these values increased with increasing the reaction temperature. When the reaction temperature was raised to 180 °C, the yield of 4-aminothioanisole increased to 99.5% and the reaction rate to 1.5 $g_{sub}\ min^{-1}\ g_{Pd}^{-1}$. It was also noted that when the temperature

Table 1
Results on the hydrogenation of sulfur-containing compounds over Pd/C catalyst.

Entry	Reactant	Product	1st run			2nd run		
			Reaction time (min)	Conversion (%)	Selectivity (%)	Reaction time (min)	Conversion (%)	Selectivity (%)
1			40	100	99.7	310	100	99.8
2			5	100	98.1	10	100	98.6
3			30	100	99.8	220	100	99.6
4			45	100	99.7	340	100	99.8
5			60	100	97.5	390	100	98.3
6			70	100	96.7	440	100	96

Reaction condition: 0.05 g Pd/C, 2.0 g substrate, 10 mL toluene, 3 MPa, 180 °C.

was increased above 120 °C, aniline became the sole byproduct most likely due to the cleavage of C—S bond of 4-aminothioanisole.

We then performed the hydrogenation of 4-nitrothioanisole over the used catalysts at the corresponding initial hydrogenation temperatures of 60, 180 and 200 °C, respectively. No hydrogenation of 4-nitrothioanisole was detected over the used catalysts at 60 °C. This is probably because the active metal sites of Pd/C were blocked by sulfur-containing molecules, inhibiting the dissociation of H_2 and the consequent migration of hydrogen atoms on the Pd surface [30]. In contrast, 4-nitrothioanisole could be completely converted into 4-aminothioanisole at 180 and 200 °C after reacting for 1100 and 850 min, respectively, but the hydrogenation rates decreased to 0.9 and 1.2 g_{sub} min^{-1} g_{Pd}^{-1} at these two respective temperatures.

After the reactions, the catalysts were characterized by XRD (Fig. 2) in order to investigate the effect of the temperature on their catalytic performance in the hydrogenation reactions. The XRD patterns showed that there was no change for the catalyst used at 60 °C since only diffraction peaks of metal Pd could be observed. Interestingly, at the reaction temperature above 120 °C, two new diffraction peaks at around 39.4° and 35.1° were observed, which are associated with Pd_4S. The formation of Pd_4S phase seemed to be more profound with higher reaction temperature and a complete transformation of Pd into Pd_4S phase was observed at 200 °C. Combining with the product analysis in Fig. 1, we discovered the phenomenon known as *in situ* sulfidation that Pd metal was sulfided by the sulfur from the substrates. The repeated experiments with the used catalysts at 180 and 200 °C revealed that the *in situ* sulfided "Pd_4S" phase was active for the hydrogenation of 4-nitrothioanisole, since 100% conversion was obtained with prolonged reaction times. Novakova et al. reported the use of the substrate-to-Pd molar ratio of 26:1 in their experiments to yield 98% after reacting for 360 min at 75 °C and claimed this molar ratio has almost reached the limit of completely poisoning the catalyst surface [15]. While in our experiments, the substrate-to-Pd mole ratio was 626:1, but the yield to final products still kept above 98.2% even after reacting for 440 min at 200 °C. The main factor causing the quite different results was temperature.

3.2. *Mechanism of* in situ *sulfidation Pd/C*

According to the XPS results (Fig. 3) of the catalyst used at 60–200 °C, the S_{2p} peaks at 163.1–163.6 and 168.6–169.3 eV were ascribed to NO_2PhSMe and sulfate (S^{6+}), respectively [31]. And a special S_{2p} peak at 164.6–164.9 eV emerged when the temperature increased to 120 °C, which was most likely attributed to S_n [32]. However, this S_{2p} peak was not detected in the XPS spectra of the catalyst used at 60 °C. Combining the XRD and XPS results, we highly believe the sulfidation process was a step-wise process which might comprise (1) C—S bond cleavage, (2) *in situ* sulfidation from point to surface and (3) finally to bulk of Pd crystal particles. Specifically, it started with the strong anchoring of

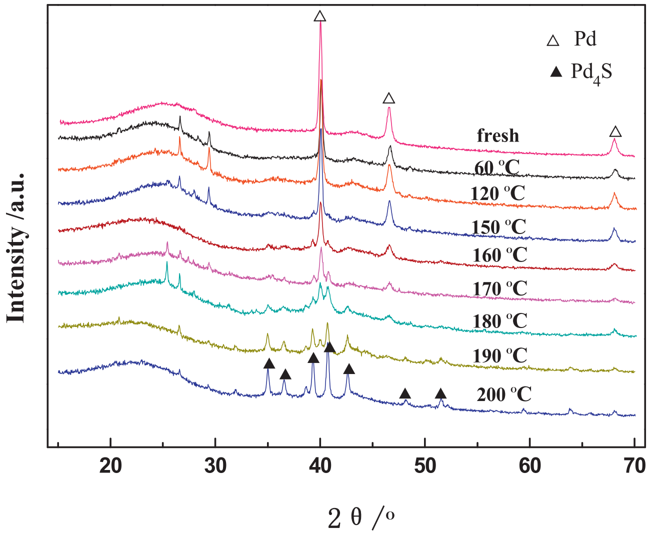


Fig. 2. The XRD patterns of spent catalysts after the hydrogenation of 4-nitrothioanisole at various temperatures. The XRD patterns of Pd and Pd_4S phases were assigned based on JCPDS PDF no. 0011201 and JCPDS PDF no. 731387, respectively.

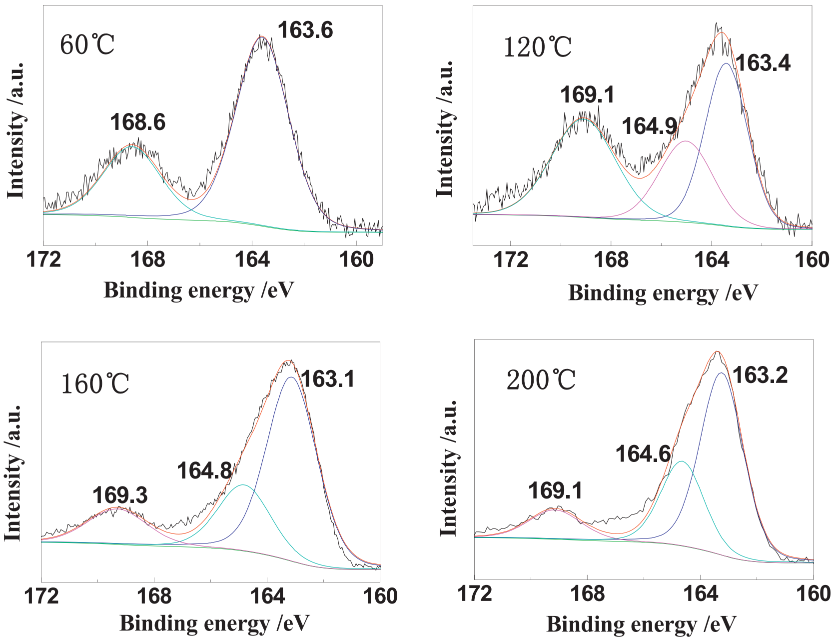


Fig. 3. XPS spectra of S 2p of the catalysts used at 60, 120, 160 and 200 °C.

sulfur-containing molecules onto the Pd surface, which modified the structure of the metal valence band by decreasing the density of states near the Fermi level at low reaction temperature [33]. Then, the cleavage of the C—S bond transpired to form NO_2PhSH, MeSH and H_2S at higher temperatures after the adsorption of sulfur-containing molecules on the surface of Pd [34,35]. Subsequently, the reaction of H_2S with surface Pd atoms took place, forming the initial sulfides with a bilayer structure (sulfide/metal) [36]. Finally, the diffusion of Pd vacancies ensued after surface sulfidation and Pd_4S was then formed [27]. Hence, it can be concluded that at 60 °C, organic sulfur compounds adsorbed on the surface of metal Pd and caused the deactivation of the catalyst. When the reaction temperature increased above 120 °C, the decomposition of the adsorbed organic sulfur compounds on the surface of metal Pd and the sufidation of Pd metal and S_n to form new active phase "Pd_4S" could be carried out [36]. As demonstrated in the repeated experiments, the catalysts after the *in situ* sulfidation process exhibited a lower activity than those used in the first run, indicating that Pd_4S has a lower activity than that of metal Pd. Meanwhile, the amount of byproduct (aniline) decreased during the recycling reactions. This is probably due to the lower activation barriers for H_2 dissociation and C—S bond cleavage on the surface of Pd_4S than that of Pd metal [27].

The hydrogenation of a series of sulfur-containing compounds other than 4-nitrothioanisole was also investigated at 180 °C and 3 MPa of H_2. As shown in Table 1, using Pd/C catalysts, and all tested reactants were converted into the corresponding products with superior yields in either first or recycling reactions. The main by-product was aniline due to the hydrodesulfurization. In addition, the hydrogenation/hydrogenolysis of dinitrodiphenyl was achieved, indicating that *in situ* sulfided Pd/C catalyst was also capable of cleaving S—S bond.

3.3. Reconstruction of Pd sulfides during recycling

It is well known that the stability of catalysts is of great importance from industrial point of view. Previous studies showed that other palladium sulfides crystalline phases including Pd_3S, $Pd_{16}S_7$ and PdS could also be formed after the complete transformation of Pd into Pd_4S. Therefore, it is necessary to investigate the phase transformation of palladium sulfides catalysts during the recycling reactions and further correlate the catalytic performance with the species of palladium sulfides. The experimental results in Fig. 4 show the catalytic performance of Pd/C in each of 18 recycles with a catalyst-to-reactant weight ratio of 1:20 at 180 °C and H_2 pressure of 3 MPa. It can be seen that the yield was maintained above 98% for each reaction. In addition, it was found that the average reaction rate decreased from 10 to 0.37 $g_{sub}\ min^{-1}\ g_{Pd}^{-1}$ in the first three recycles. The decrease of the hydrogenation rate during the recycling was similar to the result as described above. However, the catalyst activity was maintained in the reaction rate range of $0.37-0.54\ g_{sub}\ min^{-1}\ g_{Pd}^{-1}$ from the 3rd to the 18th recycling, which was much better than the results reported by Novakova et al. [15].

The XRD analysis of the recycled catalyst (Fig. 5) reveals in details how Pd sulfides reconstructed during the hydrogenation process. A complete sulfidation of metal Pd into Pd_4S was achieved after two recycling reactions as the peaks for Pd totally disappeared, and the formed Pd_4S could be observed throughout the 18 recycles.

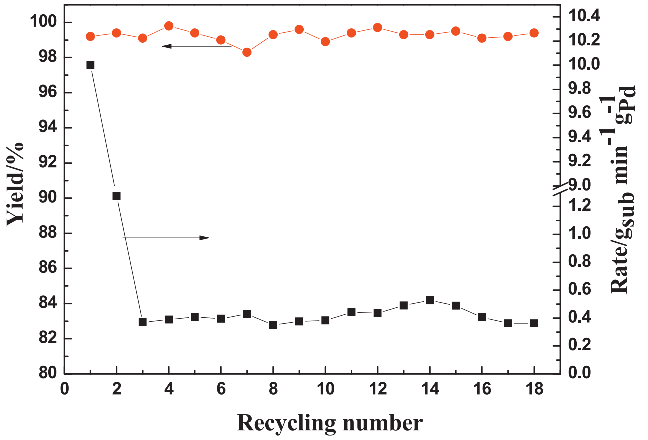


Fig. 4. The reaction rate and products yield of Pd/C catalyst against recycling number. Reaction conditions: 1 g Pd/C, 20 g 4-nitrothioanisole, 150 mL toluene, 180 °C, 3 MPa H_2.

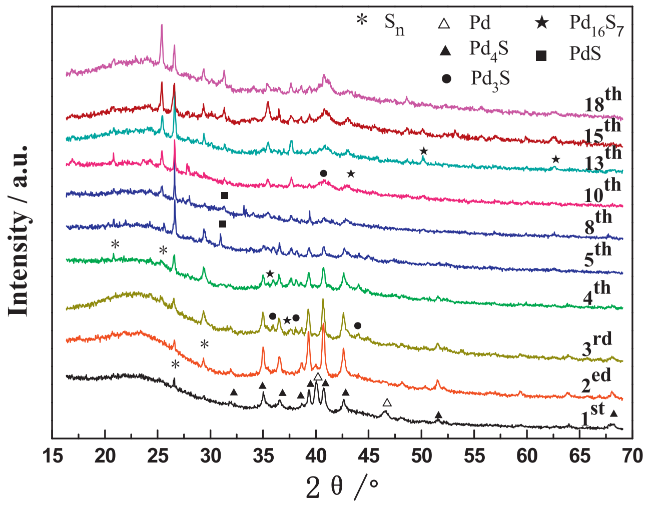


Fig. 5. The XRD patterns of the Pd/C catalyst recycled in reactions. The XRD patterns of $Pd_{16}S_7$, Pd_3S and PdS phases were assigned based on JCPDS PDF no. 752228, JCPDS PDF no. 731831 and JCPDSPDF no. 741060, respectively.

After the 3rd recycling, three new peaks at 36.0°, 38.1° and 44.1° were detected possibly due to the formation of Pd_3S, but they were gradually faded out as the recycling number increased. Meanwhile, additional peaks at 35.5°, 37.7°, 43.1° and 50.1° were observed with the increase of recycling numbers, which might associate with the transformation of Pd_3S or Pd_4S to $Pd_{16}S_7$ phase [36]. The presence of peaks at 31.1° and 34.0° indicated that only a trace amount of PdS was found after the 5th recycling. Recently, we have prepared a series of Pd_4S/C, Pd_3S/C, $Pd_{16}S_7$/C and PdS/C catalysts in our previous study [27], and found that their catalytic activities in the hydrogenation of 4-nitrothioanisole were ranked in the following order: $Pd_{16}S_7/C \geq Pd_4S/C > Pd_3S/C \gg PdS/C$ (Fig. S1). Noted that the sulfur in PdS phase is almost not mobile, which can cause its activity be much lower than that of other palladium sulfides catalysts [13]. If the metal Pd was entirely *in situ* sulfided into Pd_3S or PdS, the catalyst would be deactivated completely. On the other side, if the amounts of Pd_3S and PdS were just a few, the activity of the catalyst would be remained due to the activity of $Pd_{16}S_7$ was only a little higher than that of Pd_4S. In our experiments, a little bit of Pd_3S was detected in the 3rd recycling and then it faded out as the recycling number increased, and a trace amount of PdS was found after the 5th recycling. Although the amounts of PdS_4 and $Pd_{16}S_7$ phases were changed during the 3rd to the 18th recycling, the amounts of Pd_3S and PdS were not increased significantly. Therefore, as long as metal Pd was not entirely *in situ* sulfided into PdS, the catalyst could render a better activity and stability in the hydrogenation of sulfur-containing nitrobenzene. This should be the reason for the reaction rate was remained during the 3rd to the 18th recycling.

4. Conclusion

In this study, *in situ* sulfidation of Pd/C by sulfur-containing compounds for the preparation of Pd_xS_y/C catalyst was proposed. The *in situ* sulfided catalyst showed excellent performance in the hydrogenation of sulfur-containing nitrobenzene and there was no significant loss in the activity and yield during the recycling reactions. Both the cleavage of C—S bond of sulfur-containing reactants and the followed reaction of Pd metal with sulfur could only be initiated at higher temperatures (around 120 °C), indicating that the *in situ* sulfidation of Pd/C catalyst was highly dependent on temperature. The hydrogenation rate of sulfur-containing nitrobenzene was much higher over Pd_4S and $Pd_{16}S_7$ phases, indicating that the two phases were mainly responsible for the adsorption and the activation of H_2 and sulfur-containing compounds. The catalytic stability of the *in situ* sulfided catalyst could be attributed to the stable presence of Pd_4S and $Pd_{16}S_7$.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2015.02.043.

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