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Thermal oxidation to regenerate sulfone poisoned Pd-based catalyst: effect of the valence of sulfur

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Sulfur deactivation is a serious problem which largely limits the industrial application of noble metals as catalysts. Here we report a thermal oxidation method to regenerate sulfone poisoned Pd/C catalyst applied in the hydrogenation of sodium-*m*-nitrobenzene sulfonate (SNS). It was found that the initial activity of Pd/C catalyst could be substantially recovered after treating it in air at temperatures as low as 100 °C. And the catalyst could be reused for at least 20 times without the significant loss of activity. The properties of deactivated and regenerated catalysts were studied in detail by BET measurement, X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD), and Fourier transform infrared spectroscopy (FT-IR). The results indicated that the main surface sulfur species found on deactivated and regenerated Pd surfaces were S_n and sulfate (SO_4), respectively. The change of the valence of sulfur species was found to be the key factor influencing the catalytic activity of the Pd-based catalyst.

1. Introduction

Aminobenzene sulfonic acids, such as *m*-aminobenzenesulfonic acid (*m*-ABSA), 1-amino-8-naphthol-3,6-disulfonic acid (H-acid), and 6-chloro-3-aminotoluene-4-sulfonic acid are important dye and medicine intermediates.[1–3] They are usually prepared by the reduction of the corresponding nitrocompounds, using iron powder, hydrogen, *etc.* as reducing agents.[4] In contrast to the conventional iron-acid reduction process, the catalytic hydrogenation method using metal catalysts, such as nickel-, platinum-, and palladium-based catalysts is more environmentally friendly and can produce much higher quality products.[5] However, these catalysts suffer from the problem of sulfur poisoning caused by sulfone, which is the inevitable byproduct of the sulfonation reaction in the production process (Scheme 1).[6]

Industrial catalysts usually operate under complex conditions and suffer from deactivation caused by sulfur poisoning, carbon deposition, sintering, the blocking of the pore structure by organic polymers, *etc.*[7–11] Among which, sulfur poisoning is considered as one of the major challenges in the synthesis of an active and stable catalyst.[9–11] Removing sulfur-containing impurities in industrial reactants is one way to treat the sulfur poisoning problem and can help maintain high activity of industrial catalysts; however, this process is usually highly energy consuming.[12] The second approach is to improve the sulfur tolerance of metal catalysts. There are typically two approaches employed by researchers: (a) changing the acid-base properties of the carrier; (b) changing the electronic and structural properties of the metal particles by adding a second metal. Concerning the former, it was reported that the sulfur tolerance of metal catalysts could be greatly enhanced by using acidic supports such as zeolites.[13,14] While the resistance of bimetallic catalysts to sulfur poisoning is usually the result of decreasing the affinity of sulfur to metals through electronic effects or structural changes.[15–17] Some researchers also proposed a sulfur and hydrogen intra-particle spillover mechanism to explain the improved sulfur tolerance of bimetallic catalysts.[18] However, the activity of bimetallic catalysts in a sulfur-containing environment was still substantially lower than those operating under sulfur-free conditions.[15] Another important way to enhance sulfur tolerance is to use metal sulfides as catalysts, such as PdS_4 (ref. 19) and Rh_2S_3.[20] Though high stability of these catalysts can be achieved, their catalytic activity is very low, mostly due to the harsh reaction conditions, *e.g.* relatively high temperatures and pressures, making the process energy consuming and uneconomic.[19] Till now, it is still a big challenge to overcome the problem of sulfur poisoning. Therefore, there is an urgent requirement to find an easy and efficient method to regenerate sulfur-poisoned metal catalysts.

Pd-based catalysts have been proven to be the promising metal catalysts for their excellent catalytic performance in the hydrogenation process of nitrobenzene sulfonic acid,[12] but the information about the regeneration of sulfur-poisoned Pd catalysts is scarcer. The regeneration by thermal treatment with

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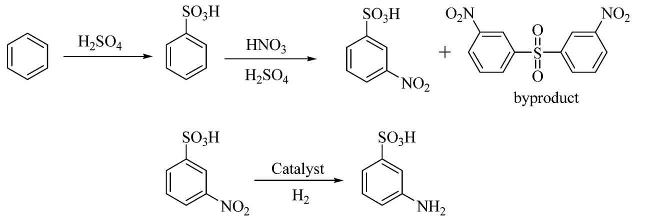


Scheme 1 Equations of synthesis of *m*-aminobenzenesulfonic acid and its following hydrogenation process.

hydrogen was reported to be useful to recover the activity of the catalysts, however the temperature used was relatively high (>400 °C).[21–24] Liquid oxidation using hydrogen peroxide (H_2O_2) or sodium hypochlorite (NaClO) as oxidants is an effective way to remove sulfur species from metal surface and has been successfully employed to recover sulfur deactivated Pd-based catalyst, in spite that the major disadvantage of this regeneration process is the production of waste water.[25,26] In addition, both the deactivation of Pd-based catalysts by sulfur and the corresponding regeneration processes have not previously been investigated in details. In comparison, thermal oxidation using air as oxidant is an ideal choice in terms of environment and economics, and the successful application of it in regenerating nickel catalyst has proven its potential in the regeneration of sulfur-poisoned metal catalysts.[7,27–30] As for palladium, only a few literature can be found on the oxidation of sulfur atoms adsorbed on Pd surface and most of the researches still stay in the theoretical stage.[31,32] Therefore, it seems adequate to try to apply thermal oxidation to regenerate sulfur poisoned Pd-based catalysts.

In this paper, we placed our interests in recovering the activity of sulfur poisoned Pd-based catalysts by thermal oxidative treatment in air and investigate the correlation between the states of sulfur species on Pd surface and the activity of Pd-based catalysts in details. We initially studied the poisoning process of 3-nitrophenyl sulfone to Pd/C catalyst for the hydrogenation of sodium-*m*-nitrobenzene sulfonate (SNS). The properties of deactivated Pd/C catalysts were then analysed by BET measurement, temperature programmed desorption (TPD) to find out the reasons for catalyst deactivation. The possible reasons for the Pd/C catalyst regenerated by thermal oxidation treatment were also discussed. Based on the results, a thermal oxidation method developed appeared to be very easy and efficient to recover sulfone-poisoned Pd/C catalyst and might be highly applicable in the regeneration of other sulfur-poisoned noble metals.

2. Experimental

2.1. Preparation of Pd/C catalyst and palladium nanoparticles

Pd/C catalyst was prepared by adding a desired volume of H_2PdCl_4 (Hangzhou Kaida Metal Catalyst & Compounds Co. Ltd.) aqueous solution ($0.05\ g_{metal}\ mL^{-1}$) into an aqueous slurry of activated carbon (C, Shaowu Xinsen Chemical Industry Co. Ltd.) support (the ratio of support to water was 1 g/10 mL) to obtain a Pd nominal loading of 5 wt%. The slurry was vigorously stirred at 80 °C for 5 h. The pH of the slurry solution was then adjusted to 8–9 by dropwise addition of NaOH aqueous solution (10%). Eventually, the precipitated $PdO \cdot H_2O$ supported on carbon was reduced by hydrazine hydrate, filtered, and dried under vacuum at 383 K overnight. The preparation of palladium nanoparticles (NPs) was done following a similar procedure.

2.2. Deactivation of Pd/C and Pd NPs by 3-nitrophenyl sulfone and their regeneration

The pretreatment of Pd NPs or Pd/C catalyst by 3-nitrophenyl sulfone was carried out in a 500 mL high-pressure stainless steel autoclave. Typically, 2.0 g of 5% Pd/C, 1.0 g of 3-nitrophenyl sulfone (Hebei Jianxin Chemical Co. Ltd.), or 0.1 g of Pd NPs, 1.0 g of sulfone (Aladdin Chemistry Co. Ltd.) and 150 mL of deionized water were introduced into the autoclave. Then the autoclave was sealed and purged with the reaction gas (N_2 or H_2 for Pd/C catalyst and H_2 for Pd NPs) for three times to remove the air inside. The reaction was carried on at 80 °C and 0.8 MPa with a stirring rate of 1100 rpm for 3 h. The Pd/C catalyst (or Pd NPs) was filtered and washed thoroughly with ethanol and deionized water, respectively. The deactivated Pd/C catalyst and Pd NPs were denoted as Pd/C–X ($X = N_2$ or H_2) and Pd NPs-H_2, respectively, where X was the reaction gas.

The regeneration experiment of Pd/C catalyst was performed by thermal treatment of the poisoned Pd/C–H_2 sample at 100 °C in different gas atmospheres for 8 h. The sample was denoted as Pd/C–H_2–Y (Y = air, Ar, H_2), where Y was the regeneration gas. The Pd/C catalyst deactivated during the hydrogenation of industrial SNS was treated only in air at 100 °C. The Pd/C–H_2 catalyst thermally treated in air at different temperatures were denoted as Pd/C–H_2–air–Z, where Z was the temperature (°C) used.

2.3. Catalytic tests

The SNS hydrogenation reaction was carried out in a 500 mL stainless steel autoclave. Typically, 0.2 g of 5% Pd/C catalyst, 20.0 g of SNS and 100 mL of deionized water were fed into the reactor. The autoclave was sealed and purged by H_2 gas for three times. The reaction was performed under the hydrogen pressure of 0.6–0.8 MPa at 80 °C with the stirring rate at 1100 rpm. After the reaction, the Pd/C catalyst was filtered and washed with deionized water several times. The products were analyzed by liquid chromatography (Agilent 1100 series) equipped with a UV detector (wavelength, 230 nm), and 0.5% $(NH_4)_2CO_3$ (pH = 6) solution was used as the mobile phase.

The hydrogenation of sulfone was carried out in a 500 mL stainless steel autoclave. In a typical experiment, the 5%Pd/C catalyst, sulfone, and solvent were fed into the reactor. The reaction conditions were the same as that of SNS hydrogenation. And the liquid products were analyzed by GC-MS (Agilent 6890GC-5973 MS equipped with a 25 *m*-HP-5 capillary column, MS detector). The sulfur containing compounds both in liquid and gas products were also monitored by online GC (Fu Li 9790

GC equipped with a 30 *m*-FFAP capillary column, FPD detector, detection limit: 0.1 ppm).

2.4. Catalyst characterizations

The BET surface area and porous parameters of the Pd/C catalysts were determined by nitrogen physical adsorption–desorption at −196 °C. In a typical experiment, a 50 mg sample was heated to 180 °C and held for 12 h to remove the adsorbed species. Nitrogen adsorption isotherm was measured using a NOVA 1000e surface area analyzer (Quantachrome Instruments Corp.). X-ray diffraction (XRD) measurements of the Pd/C catalysts were performed using an X'Pert diffractometer (PNAlytical Co.) equipped with a Cu K radiation source that was operated at 60 kV and 55 mA. XPS spectroscopy analyses were performed with a Kratos AXIS Ultra DLD instrument. Al Kα radiation at an energy scale calibrated *versus* adventitious carbon (C1s peak at 284.6 eV) was used. The surface compositions of the samples were determined from the peak areas of the corresponding origin fitting lines.

In order to eliminate the interference of carbon support, palladium nanoparticles (Pd NPs) were prepared and used for Fourier transform infrared (FT-IR) analysis. The FT-IR spectroscopy of Pd NPs was recorded by a Necolet 6700 spectrometer. The Pd NPs–H_2 sample was diluted in KBr pressed into pellets, and pressed into tablets. The regeneration of Pd NPs–H_2 was performed by heating the pellets at 100 °C under air for 8, 12 h, respectively. All FT-IR spectras were recorded with 64 scans at a resolution of 4 cm^{-1}.

The TPD experiment with sulfone deactivated Pd/C catalyst was carried out in a flow setup operating at atmospheric pressure in helium. The gas composition leaving the reactor was monitored by an online mass spectrometer (Omnistar). In a typical measurement, 100 mg of Pd/C catalyst was loaded into a tubular quartz reactor with an inner diameter of 20 mm. The catalyst was first dried at 80 °C for 30 min in flowing helium. Subsequently, the catalyst was heated in helium at a flow rate of 30 mL min^{-1} with a heating ramp of 10°C min^{-1}, and the products were monitored by the online MS.

3. Results and discussion

3.1. Transformation of 3-nitrophenyl sulfone and Pd/C deactivation

3-Nitrophenyl sulfone is an inevitable byproduct during the synthesis of *m*-nitrobenzene sulfonic acid (*m*-NBSA) and it is the main sulfur-impurity remaining in industrial reactant before the hydrogenation process. In order to investigate its effect on the activity of Pd/C catalyst, chemically pure grade of reactant (CP, 99%) was employed to compare with industrial reactant (IN), the results are shown in Fig. 1. For analytical reactant (CP, 99%), the average reaction rates of Pd/C catalyst over three continuous runs were 7.40, 6.73, 5.70 mmol g_{Pd}^{-1} s^{-1}, respectively, indicating good performance. Upon the addition of 3-nitrophenyl sulfone (CP + Sulfone), the average reaction rate of Pd/C catalyst decreased dramatically similar to the behavior of the catalysts with industrial reactant. So that it is reasonable to assume that 3-nitrophenyl sulfone is the main cause behind the severe deactivation of Pd/C catalyst in industrial application.

Some studies pointed out that 3-nitrophenyl sulfone itself could not poison metal catalysts extensively as the sulfur atom was believed to be totally shielded by oxygen.[26,33] Therefore, we suspect that there might be certain reactions happened between 3-nitrophenyl sulfone and hydrogen over Pd/C catalyst. To verify our hypothesis, Pd/C catalyst was pretreated with 3-nitrophenyl sulfone under N_2 (Pd/C–N_2) and H_2 (Pd/C–H_2) as comparison. In Fig. 2, we can see that the initial activity of Pd/C catalyst was only influenced significantly by the pretreatment in H_2 (~14.5% of fresh Pd/C), also suggesting that the adsorbed 3-nitrophenyl sulfone itself was not enough to poison the catalyst. Therefore it was likely that a new sulfur species was produced by the reaction between 3-nitrophenyl sulfone and H_2 over Pd/C catalyst.

To further investigate the transformation of sulfone, the hydrogenation of sulfone over Pd/C catalyst was performed (Table 1). Aniline, cyclohexylamine for 3-nitrophenyl sulfone (entry 1 and 2) and benzene, cyclohexane for sulfone (entry 3 and 4) products were observed, indicating the hydrogenolysis of C–S bond over Pd/C catalyst. Due to the strong conjugation between $S{=}O$ and $C{=}C$ of benzene ring in sulfone, the direct cleavage of C–S bond in sulfone was considered to be difficult.[33–35] Thus to better understand the hydrogenolysis process, the sulfur-containing products both in liquid and gas phases were further analyzed for entry 4 as a representative by GC-FPD (flame photometric detector). In the liquid phase, the only detected sulfur species was cyclohexylsulfonylbenzene (Scheme 2) and its structure was confirmed by GC-MS. The results indicated that the hydrogenolysis process of sulfone over Pd/C catalyst may be as follows: (1) the hydrogenation of one of the benzene ring in sulfone to form cyclohexylsulfonylbenzene, therefore the conjugative structure between $S{=}O$ and $C{=}C$ of

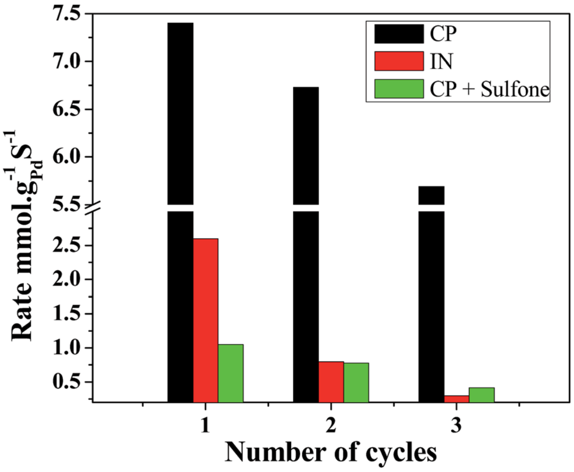


Fig. 1 Effect of 3-nitrophenyl sulfone on the activity of Pd/C catalyst used for the hydrogenation of SNS. CP: chemically pure grade of reactant (99%), IN: industrial reactant, CP + sulfone: chemically pure grade of reactant (99%) with 0.5% mass ratio of 3-nitrophenyl sulfone (reaction conditions: 0.2 g cat., 20.0 g SNS, 100 mL H_2O, 80 °C, 0.6–0.8 MPa H_2, 1100 rpm).

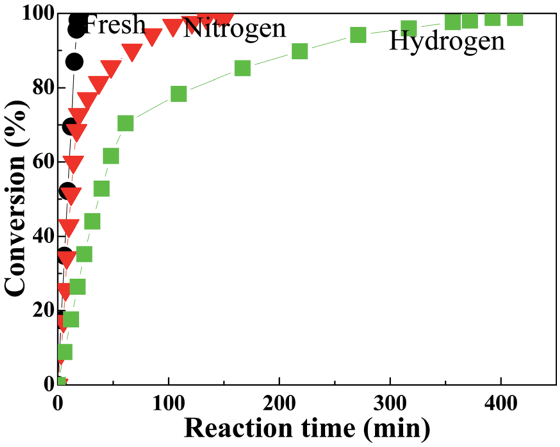
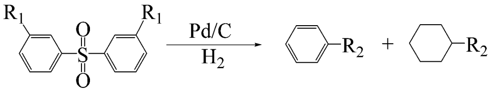
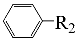
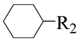


Fig. 2 Conversion as a function of reaction time of SNS hydrogenation over Pd/C catalysts pretreated with 3-nitrophenyl sulfone in N_2 and H_2 (reaction conditions: 0.2 g cat., 20.0 g chemically pure grade of SNS (99%), 100 mL H_2O, 80 °C, 0.6–0.8 MPa H_2, 1100 rpm).

Table 1 Liquid products distribution of the hydrogenation of sulfone over Pd/C catalyst[a]

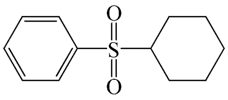


	Sulfone			Products distribution (%)			
Entry	R_1	R_2	Cat./sub. (g g^{-1})	Substrate			Others
(1)	NO_2	NH_2	0.2	93.3	0.9	0.1	5.7
(2)	NO_2	NH_2	10	78.5	0.3	0.4	20.8
(3)	H	H	0.2	98.1	0.1	–	1.8
(4)	H	H	20	9.9	10.7	2.1	77.3

[a] Reactions conditions: 80 °C, 120 mL THF, 0.8 MPa hydrogen with (1) 0.2 g cat., 1.0 g substrate, 3 h; (2) 2.0 g cat.,0.2 g substrate, 10.34 h; (3) 0.2 g cat., 1.0 g substrate, 6 h; and (4) 2.0 g cat., 0.1 g substrate, 6 h.

benzene ring was destroyed; (2) the cleavage of C–S bond in cyclohexylsulfonylbenzene to form benzene and cyclohexane. In the gas phase, no sulfur species (for example H_2S, SO_2) was detected even though FPD detector with very low detection limit (0.1 ppm) was used. This finding implied that only one C–S bond in sulfone was broken over Pd/C catalyst to form sulfur species.

3.2 Analysis of physiochemical properties of deactivated Pd/C catalyst. Generally speaking, the catalyst deactivation is often caused by the sintering of metal particles, the blocking of pore structure by organic polymers, and/or the coverage of active sites by strong adsorbents, such as sulfur.[7,8,36] To get clear insight into the deactivation process of Pd/C catalyst, the properties of fresh and poisoned catalysts were analyzed through BET, XRD, and He-TPD.



Scheme 2 Formula of cyclohexylsulfonylbenzen

3.2.1 BET. As shown in Table 2, both the surface areas and the corresponding pore volumes of CP-Pd/C and Sulfone-Pd/C catalysts illustrated an obvious decrease trend compared with fresh Pd/C, indicating that organic substances, such as the products, were accumulated in the pores of carbon support once used. This might be the cause of the decrease in the activity of the fresh catalyst with subsequent recycles (Fig. 1). But the physical properties (surface area and pore volume) of the spent catalysts (CP–Pd/C and sulfone–Pd/C) were similar. In fact, CP–Pd/C catalyst showed good activity and excellent recycling performance (as shown in Fig. 1) for the hydrogenation of SNS. Therefore, the deactivation of Pd/C catalyst caused by 3-nitrophenyl sulfone could not be simply ascribed to the loss of surface area and pore volume.

3.2.2 XRD. The Pd particle size of fresh and sulfone deactivated Pd/C catalysts were characterized by XRD to determine the change in the structure and the growth of crystallite. Fig. 3 also showed XRD patterns of fresh and sulfone deactivated Pd/C catalysts. Three diffraction peaks at ~39.9, 46.7, and 68.2° correspond to the (111), (200), and (220) planes of face-centered cubic (fcc) structure crystalline Pd, respectively.[37] It should be noted that no significant reflection shift in XRD was observed for the sulfone deactivated Pd/C catalyst, which might be attributed to the relatively low amount of unsaturated sulfur species.[18] The Pd particle size determined by XRD for fresh and sulfone Pd/C catalyst was 14.4 and 14.2 nm, indicating no significant sintering of palladium crystallites for the sulfone deactivated catalyst.

3.2.3 He-TPD. We have pointed out in 3.1 that the hydrogenolysis of sulfone would generate sulfur-containing compounds. In order to understand the interaction between sulfur fragments and palladium surface, the sulfone deactivated Pd/C catalyst was characterized by He-TPD. As exemplified in Fig. 4, C_6H_6, associated to the relative mass $m/z = 78$, and SO_2, corresponding to $m/z = 64$, were detected at exactly the same temperature (~330 °C). The results indicated that the generation of C_6H_6 and SO_2 might be attributed to the thermal decomposition of benzene sulfinic acid. In addition, peaks of thiophenol ($m/z = 110$), hydrogen sulfide ($m/z = 34$) and cyclohexane ($m/z = 84$) and cyclohexanethiol ($m/z = 116$) were also detected in TPD experiment. The results further confirmed

Table 2 Physicochemical properties of Pd/C catalyst

Sample	S_{BET} (m^2 g^{-1})	V_{pore} (cm^3 g^{-1})	Pd[c] (wt%)	d_{Pd}[d] (nm)
Fresh-Pd/C	1936	1.217	4.7	14.4
CP-Pd/C[a]	1277	0.843	4.5	14.5
Sulfone-Pd/C[b]	1297	0.846	4.6	14.2

[a] Spent catalyst for CP reactant. [b] Spent catalyst for CP reactant with 3-nitrophenyl sulfone. [c] Determined by ICP-MS. [d] Determined by XRD.

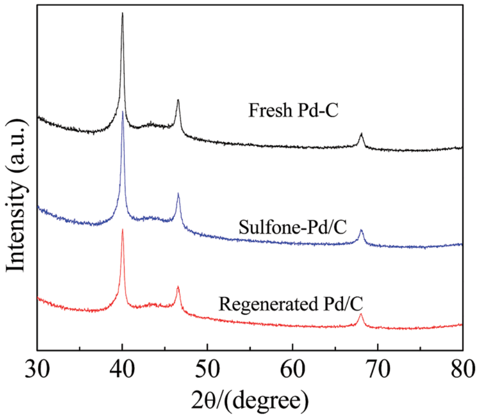


Fig. 3 XRD patterns of (a) fresh, (b) sulfone deactivated Pd/C, (c) regenerated Pd/C catalysts. The regeneration was conducted by thermally treated in air at 100 °C for 8 h.

that sulfone was reduced on palladium surface by the cleavage of C–S bond. The cleavage of C–S bond of sulfone resulted in the formation of benzene sulfinic acid, and the further hydrogenation process would form thiophenol and hydrogen sulfide *etc.*, as shown in Scheme 3.

With these information, the nature of Pd/C catalyst deactivated by sulfone may be concluded as follows: the active sites were blocked by coordinatively unsaturated sulfur species (such as benzene sulfinic acid, thiophenol and hydrogen sulfide by cleavage of C–S bond in sulfone), which were strongly chemisorbed on the metal surface, resulting in the deactivation of the Pd/C catalyst.

3.3 Pd/C catalyst regenerated by thermal oxidation

Based on the analysis above, we have clarified that the strong adsorption of sulfur species on Pd surface is the main reason that causes the deactivation of Pd/C catalyst. Therefore the key to regenerate sulfone-poisoned Pd/C catalyst is the removal of sulfur species from Pd surface. According to literatures, the poisoning ability to metal catalysts can be largely weakened once sulfur atom occupied by oxygen.[26,36,38]

With these considerations, a novel thermal oxidation method was adopted to recover the activity of sulfone-poisoned Pd/C catalyst (see Fig. 5). The initial activity of 3-nitrophenyl sulfone deactivated Pd/C catalyst (Pd/C–H_2) was recovered completely after thermally treated in air at 100 °C. In addition, the reaction time was largely shortened from 413 min (Pd/C–H_2) to 105 min (Pd/C–H_2–air), indicating that the thermal oxidation method was effective to regenerate 3-nitrophenyl sulfone deactivated Pd/C catalyst.

3.3.1 Role of temperature in recovering sulfone-poisoned Pd/C. As for sulfur deactivated Ni-based catalyst, the temperature required for regeneration by controllable oxidation was relatively high (~800 °C), which was related to the high activation energy of the sulfur oxidation.[7] The activation energy of the sulfur oxidation on Pd is much lower than that on Ni.[32,38] Gotterbarm *et al.* found out that sulfur atom could be removed from Pd surface between 127 and 227 °C.[32] Therefore, it is reasonable that thermal oxidation to recover the 3-nitrophenyl sulfone deactivated Pd/C catalyst can be operated at low temperatures.

In this regard, low temperatures (60–120 °C) were employed to treat 3-nitrophenyl sulfone deactivated Pd/C catalyst (Pd/C–H_2) in air and their effect on the recovered catalyst activity was shown in Fig. 6. When the temperature adopted was as low as 60 °C (Pd/C–H_2–air-60), no recovery sign could be seen on the activity of catalyst as compared to that of untreated poisoned catalyst (Pd/C–H_2, see Fig. 5). However, the activity of Pd/C–H_2 catalyst could be significantly increased as the temperature increased to 80 °C and further to 100 °C. When the temperature was >100 °C, the initial activity of Pd/C–H_2 was substantially recovered. And further increasing the treated temperature to 120 °C would not dramatically influence the activity. Therefore, the temperature as low as 100 °C seems to be enough for the regeneration of sulfone-poisoned Pd/C catalyst.

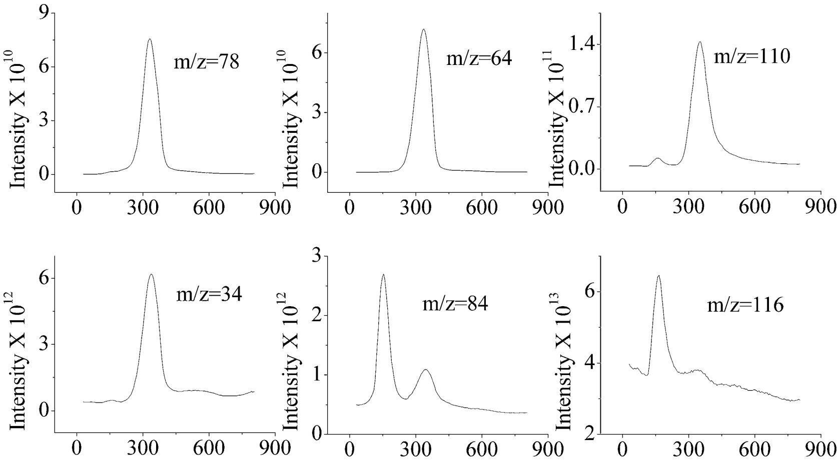
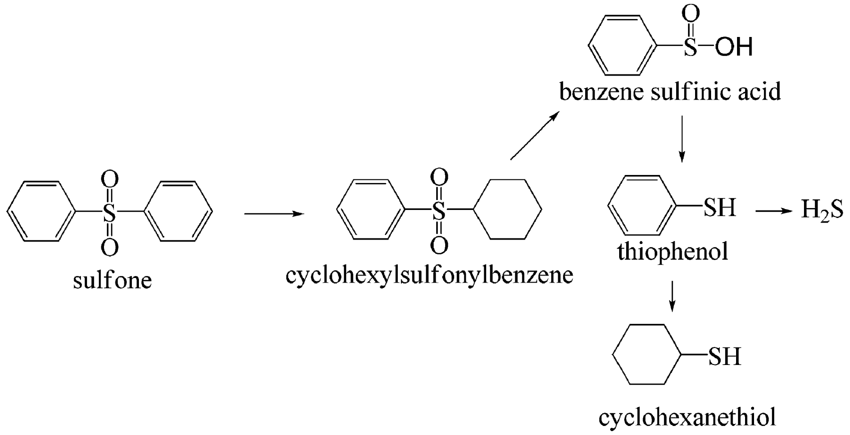


Fig. 4 TPD profiles of Sulfone-Pd/C catalyst.



Scheme 3 Possible pathways for sulfone transformation over Pd/C catalyst.

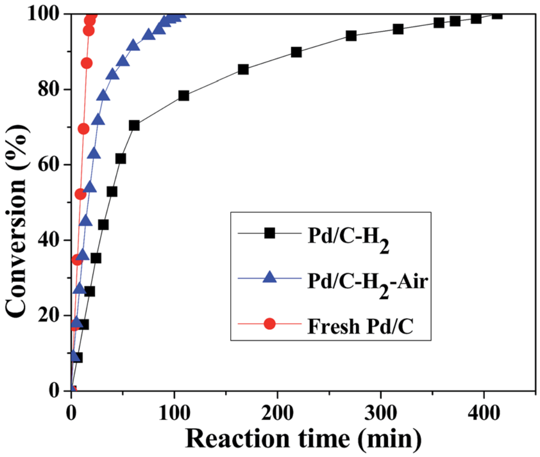


Fig. 5 The regeneration performance of 3-nitrophenyl sulfone deactivated Pd/C catalyst (Pd/C–H_2) by thermally treated in air at 100 °C for 8 h (Pd/C–H_2–air) (reaction conditions identical to those shown in Fig. 2).

3.3.2 Role of air in recovering sulfone-poisoned Pd/C. As reported, thermal treatment in inert atmosphere or reductive atmosphere have been employed to recover the activity of sulfur-deactivated metal catalysts.[27,28,39] In our work, Ar and H_2 were compared with oxidative atmosphere (air) to study the influence of treatment atmospheres on the regeneration of deactivated Pd/C catalyst (Pd/C–H_2) (Fig. 7). It can be found that Pd/C–H_2 catalyst thermally treated in air could substantially recover its initial activity. The activity of catalyst thermally treated in Ar (Pd/C–H_2–Ar), nevertheless, was almost identical to that of untreated sample (see Fig. 5, Pd/C–H_2). This is in agreement with previous study by Monzón *et al.*[39] who found a similar behavior for H_2S poisoned Pd surfaces. It was likely due to the strong bonding between sulfur and metallic sites, thermal treatment without the aid of oxygen was not sufficient to remove sulfur species from metal surface for the reactivation to happen.

Pd/C catalyst regenerated under H_2 atmosphere (Pd/C–H_2–H_2) showed even lower activity. It was reported that the

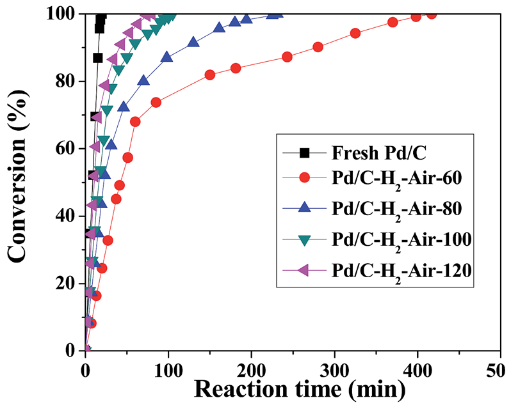


Fig. 6 Effect of treated temperature on the performance of 3-nitrophenyl sulfone deactivated Pd/C catalyst (Pd/C–H_2) for the hydrogenation of SNS (the Pd/C–H_2 catalyst was thermally treated in air at 60–120 °C for 8 h, reaction conditions identical to those shown in Fig. 2).

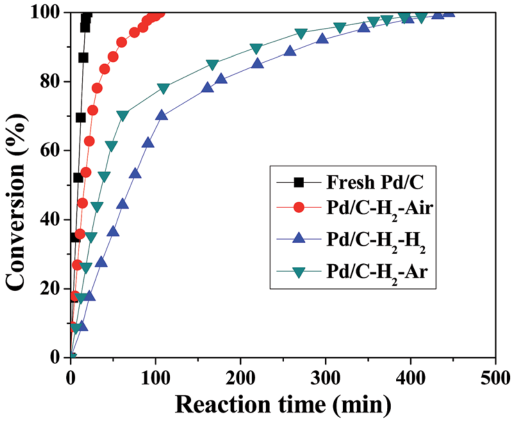


Fig. 7 Effect of treated atmospheres on the performance of 3-nitrophenyl sulfone deactivated Pd/C catalyst (Pd/C–H_2) for the hydrogenation of SNS (the Pd/C–H_2 catalyst was thermally treated in air, Ar, and hydrogen at 100 °C for 8 h, reaction conditions identical to those shown in Fig. 2).

temperatures required for the regeneration of sulfur poisoned Pd-based catalysts in H_2 was >400 °C.[21,22] The H_2–TPR results published in our recent paper confirmed that sulfur species on Pd were reduced by hydrogen and released as the form of H_2S between ∼327 and 450 °C.[19] The temperature we used here was only 100 °C, so it was difficult to remove sulfur species from metal surface. Instead, the new sulfur species formed in the reduction of 3-nitrophenyl sulfone by H_2 in low temperatures could further deteriorate Pd/C catalysts as discussed in Section 3.1.

The thermal treatment method of regenerating of sulfone-poisoned Pd/C using air as reaction atmosphere has considerable advantages over H_2 atmosphere. Firstly, the supply of air is abundant, making this method more economic. Secondly, low temperature adopted can squeeze energy usage and avoid the sintering of metal particles more effectively.

In order to study the role of air in the regeneration process, the deactivated and regenerated Pd/C catalysts were further studied by XPS (Fig. 8) and FT-IR (Fig. 9). As no water vapor was allowed in XPS and FT-IR measurement, the deactivated sample dried in Ar was taken as the best representative of the deactivated Pd/C catalyst.

The Pd $3d_{5/2}$ XPS peaks of deactivated catalyst thermally treated in Ar (Pd/C–H_2–Ar) could be deconvoluted into two peaks, namely, metallic palladium (BE at 335.4 eV) and palladium bonded with S_n & S^{6+} (BE at 336.7 eV).[19,40] But the Pd $3d_{5/2}$ XPS peaks of Pd/C–H_2–air appeared to be quite different: a new peak at 336.1 eV which could be assigned to oxidic palladium[40] had replaced the peak of PdS_x. It means the sulfur species on palladium surface was occupied by oxygen after thermally treated in air. The removal of sulfur species from palladium surface is accounted for the almost complete recovery of initial activity of Pd/C catalyst.

As shown in Fig. 9, no sulfur related group was visible for Pd NPs treated in Ar, which might be caused by the relatively weak vibrational signal of sulfur containing groups. A strong band of ∼1375 cm^{-1} was clearly visible after thermal treatment of Pd NPs in air, corresponding to the asymmetric SO_2 stretching in coordinative saturated groups, such as SO_3H groups.[41] The appearance of SO_2 stretching clearly indicates that the sulfur atoms accessible were coordinated by oxygen, which largely weakened the interaction between Pd and sulfur.

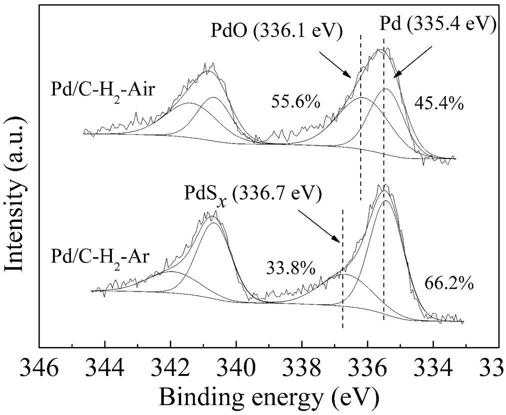


Fig. 8 XPS spectra of Pd/C–H_2 catalysts regenerated under different atmospheres. The temperature chosen for treatment was 100 °C.

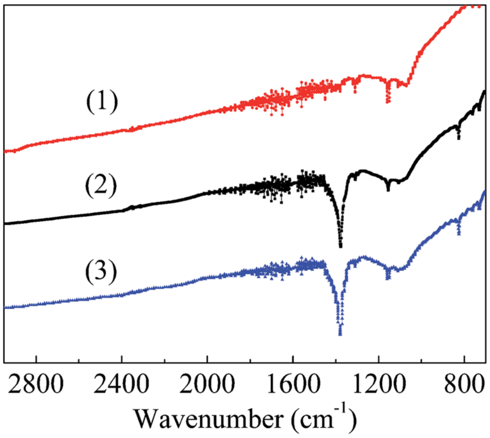


Fig. 9 FT-IR spectras of sulfone deactivated Pd NPs (1) thermally treated at 100 °C in Ar for 8 h and Pd NPs thermally treated at 100 °C in air for (2) 8 h, and (3) 12 h.

3.3.3 Recycling of regenerated Pd/C catalyst. The stability of Pd/C catalyst regenerated by thermal oxidation was also tested for the hydrogenation of SNS. After each run, the catalyst was cleaned by deionized water thoroughly and then treated in air at 100 °C for 4 h to recover its activity before reused with fresh reaction mixture in a subsequent run. As shown in Fig. 10, the activity of Pd/C catalyst slightly dropped in the first few runs and remained quite steady afterwards. The regenerated Pd/C catalyst were successfully recycled for at least 20 times without significant loss of the activity and kept 100% of SNS conversion.

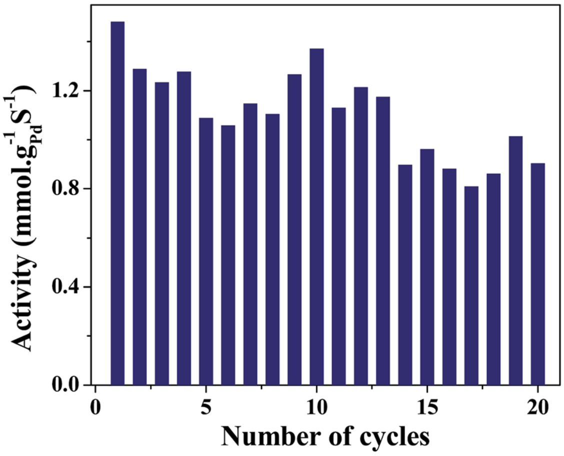


Fig. 10 Recycling performance of regenerated Pd/C catalyst used for the hydrogenation of SNS. Reaction conditions: 1.31 g 5%Pd/C, 131 g industrial SNS, 200 g H_2O, 90 °C, 0.8 MPa H_2, 1100 rpm. The Pd/C catalyst was thermally treated in air at 100 °C for 4 h before next cycle.

4. Conclusions

Thermal oxidation was able to recover sulfone deactivated Pd/C catalyst successfully at temperatures as low as 100 °C. The main reason for the catalyst deactivation was the blockage of metal active sites by low valence sulfur species derived from the hydrogenolysis of 3-nitrophenyl sulfone. The recovery of catalytic activity was attributed to the formation of high valence sulfur species with the occupation of oxygen under heating, which largely weakened the strength of Pd–S bond. In this regard, thermal oxidation method might be highly applicable in the regeneration of other sulfur-poisoned noble metals. Furthermore, we found that the regenerated Pd/C could be recycled for at least 20 times with reasonable loss of activity, so that thermal oxidation method has good prospects for the industrialization.

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