



Hydrogenation of *o*-chloronitrobenzene on a Pd/C catalyst doped with metal oxide nanoparticles

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ARTICLE INFO

Article history:

Received 8 November 2007

Received in revised form 6 April 2008

Accepted 10 April 2008

Keywords:

Pd/C catalyst

Nanoparticles

2,2'-Dichlorohydrazobenzene

Hydrogenation

ABSTRACT

Pd/C catalysts doped with cerium oxide and iron oxide nanoparticles were prepared by thermal decarboxylation in the presence of cetyl sulfonate, and used in the hydrogenation of *o*-chloronitrobenzene to give high yields of 2,2'-dichlorohydrazobenzene. It was found that the stability and activity of the Pd/C catalysts were significantly affected by doping with the nanosized metal oxides. The chemical structure of 2,2'-dichlorohydrazobenzene was confirmed by ¹H and ¹³C NMR spectroscopy.

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1. Introduction

The hydrogenation of nitro compounds is commonly conducted to prepare aromatic amines that are important intermediates for dyes, drugs, and agrochemicals. Palladium (Pd) is considered one of the best catalysts for catalytic hydrogenation of nitro compounds and it is known that the conversion of *o*-chloronitrobenzene to 2,2'-dichlorohydrazobenzene is a key step in the synthesis of key diarylide pigment intermediate 3,3'-dichlorobenzidine, which is formed by acid catalyzed rearrangement of 2,2'-dichlorohydrazobenzene [1,2]. Ideally, hydrogenation of the nitro group takes place without hydrogenolysis of the C–Cl bond [3]. Vollheim et al. reported the use of a Pd/C catalyst pretreated with a sulfoxide to hydrogenate *o*-chloronitrobenzene [4]. The goal of the pretreatment process was a catalyst giving selective hydrogenation of chloronitro-aromatic compounds. In a recent study, it was suggested that Pd–Pt colloidal alloys protected by a polymer such as polyvinylpyrrolidone (PVP) accelerated the reaction rate and significantly improved the hydrogenation of *o*-chloronitrobenzene [5,6] and gave high activity and selectivity.

We have reported that Pd/C catalysts exhibit significant variations in catalytic hydrogenation of *o*-chloronitrobenzene [7]. Results from our previous investigation showed that the hydrogenation of *o*-chloronitrobenzene to 2,2'-dichloroazoxybenzene

with Pd/C catalysts involves stages that occur at 55 and 75 °C. However, the selectivity was found to be different with new Pd/C and the used Pd/C catalyst, respectively. From the preceding, it could be concluded that the growth of the Pd particles is one of the most important contributing factors to thermal degradation and Pd sintering into large particles after high temperature aging [8–10].

Recently, it was reported that the Pd/CeO₂ catalysts exhibit much higher activity for methanol synthesis than the conventional Cu-based catalysts [11]. These high catalytic activities are attributed to the presence of cationic Pd species due to the strong contact between Pd and ceria, which significantly depends on the temperature of reduction [12]. It is well known that metal oxide nanoparticles (cerium oxide and iron oxide) and Pd-based catalysts were used for ethanol steam reforming [11,13]. However, the use of these catalysts for the hydrogenation of *o*-chloronitrobenzene to 2,2'-dichloroazoxybenzene is limited.

Nanosized metals and their oxides have been investigated for the unique physical, chemical and biological properties arising from the reduction of their sizes [14–16]. In this regard, several methods for the synthesis of iron oxide (Fe₂O₃) nanoparticles have been developed, especially in liquid phase. In most cases, capping ligands (usually organic compounds) were used to prevent small particles from agglomerating during synthesis. However, the presence of organic species restricts their applications after preparation. For example, in the field of catalysis, the removal of capping ligands from nanoparticulate surfaces was necessary to minimize the blocking of active sites [17]. The ideal capping ligands are easily removed to minimize particle growth and loss of surface area, an

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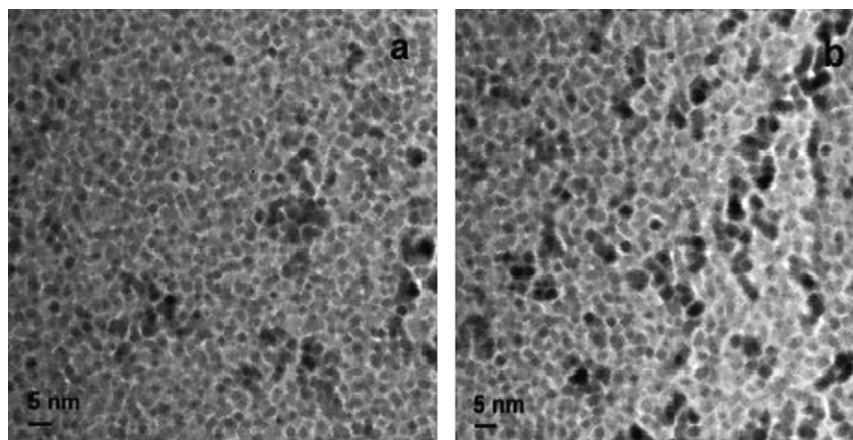


Fig. 1. TEM images of the nanoparticles of (a) Fe_3O_4 and (b) CeO_2 .

example of which is the carboxymethylsulfonyl group [18]. The effectiveness of this group is due to ease of decarboxylation at lower temperatures arising from the presence of two electron-withdrawing groups. Compounds with a carboxymethylsulfonyl group have been used to give temporary water solubility to disperse dyes and medicinal agents [19,20]. Pan et al. developed a series of temporarily water-soluble disperse dyes and intermediates containing a carboxymethylsulfonyl group. The resultant dyes underwent decarboxylation in the dye bath at elevated temperatures [21].

Taking into account the advantages to using a carboxymethylsulfonyl group, this paper pertains to the development of a new method for preparing uncoated Fe_2O_3 and cerium oxide (CeO_2) nanoparticles by thermal decarboxylation and their use in modifying Pd/C catalysts. The characteristics of metal oxide nanoparticles (cerium oxide and iron oxide) and Pd-based catalysts were analyzed by means of X-ray diffraction (XRD) and transmission electron microscope (TEM). The resultant catalysts were used in the hydrogenation of *o*-chloronitrobenzene to give 2,2'-dichlorohydrazobenzene and the effects of Pd/C modification on the activity and stability of the catalyst were also investigated. The present study is aimed at developing ways to overcome the difficulties encountered with C as supports.

2. Experimental

2.1. General

All chemicals were obtained from Jilin Chemicals Ltd. (China) in analytical grade and were used without further purification. XRD measurements were performed on a Rigaku D/max 2400 X-ray diffractometer with Cu $K\alpha$ radiation. TEM images were taken on a FEI Tecnai 20 transmission electron microscope with an accelerating voltage of 200 kV. ^1H and ^{13}C NMR spectra were recorded on Varian INOVA-400 NMR spectrometer. HPLC analysis of reaction products was conducted using an Agilent 1100 chromatographic system (Waldbronn, Germany) equipped with a diode-array detector at 254 nm. Samples were dissolved in the mobile phase (methanol/ H_2O = 80/20, v/v) and 20 μl of the sample was injected. Hypersil ODS stainless steel columns (250 mm \times 4.5 mm, particle size 5 μm) were employed.

2.2. Preparation of catalysts

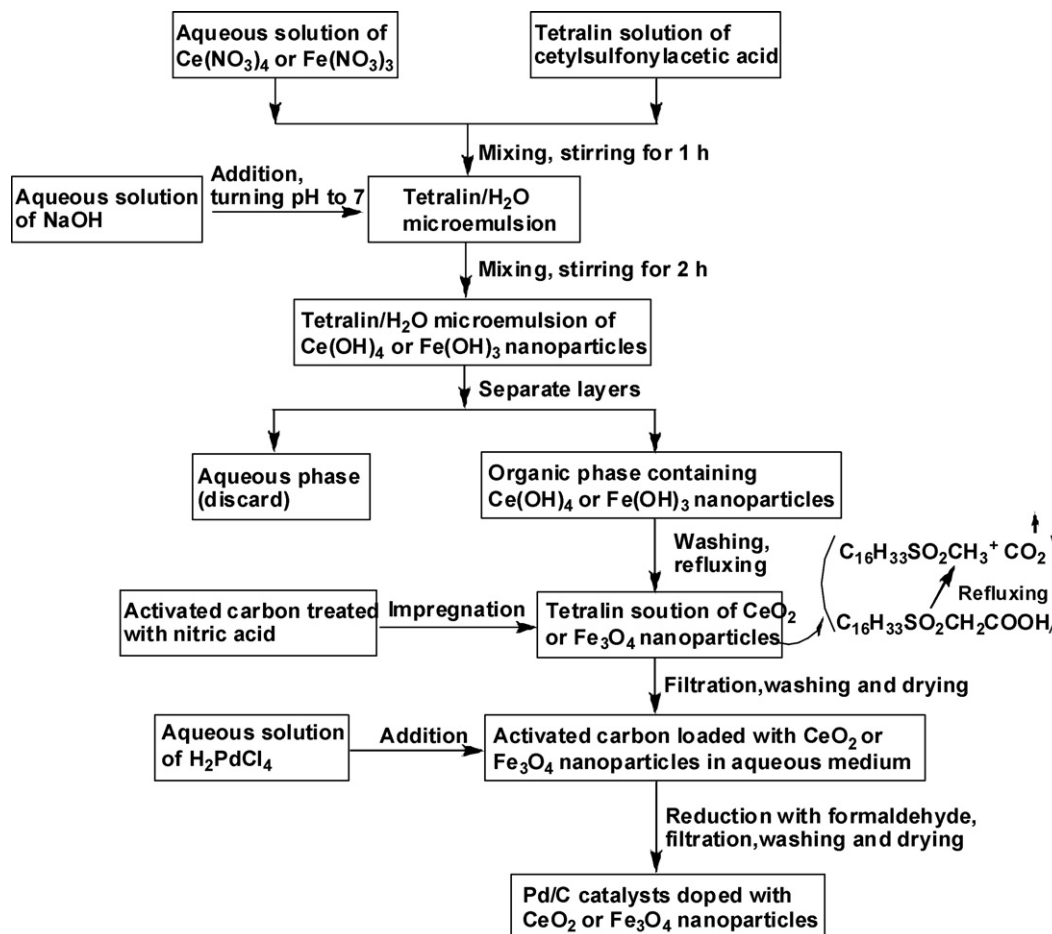
Cerium oxide (CeO_2) and iron oxide (Fe_2O_3) nanoparticles capped with cetylsulfonylacetic acid were prepared as previ-

ously reported [7]. A summary of the procedures used is as follows: nanometer-sized CeO_2 or Fe_2O_3 samples were prepared by the microemulsion method. Aqueous solution of $\text{Fe}(\text{NO}_3)_3$ (25 g, 0.1 mol/l) or $\text{Ce}(\text{NO}_3)_4$ was added to tetralin (150 ml) containing cetylsulfonylacetic acid (0.9 g), stirred at room temperature to form a microemulsion, and NaOH (70 ml, 0.1 mol/l) was added. After stirring 60 min, the product had entered the organic phase and the reaction system was allowed to stand until the phases separated. The aqueous phase was discarded and the organic phase was stirred under reflux for 0.5 h, then let stand at room temperature. The small amount of water on the bottom of the flask was discarded and the organic phase was washed several times with distilled water to give a solution of nanometer-sized CeO_2 or Fe_2O_3 .

Activated carbon (1.5 g) was stirred for 2 h with HNO_3 (10 ml, 65%) at 80 $^\circ\text{C}$ and then dried overnight at 110 $^\circ\text{C}$. The resultant activated carbon was added to the organic phase prepared above, stirred for 2 h at 80 $^\circ\text{C}$, and the solid was collected, washed with petroleum ether, and dried. The solid was added to a solution of H_2PdCl_4 (10 ml, 5 g/l), stirred with formaldehyde (10 ml, 37%) for 3 h at 60 $^\circ\text{C}$, and collected by filtration. The ratios of Pd to CeO_2 or Fe_2O_3 were controlled by the stoichiometry of the process.

2.3. Hydrogenation of *o*-chloronitrobenzene

To a 200 ml stainless steel autoclave *o*-chloronitrobenzene (30 g, 0.19 mol), NaOH (30 g, 25%, w/w, 0.188 mol), 1% Pd/C (0.6 g), and toluene (30 g) were added. After the system was flushed with nitrogen, hydrogenation was performed for 4–6 h min. at 55 $^\circ\text{C}$ with vigorous stirring under a hydrogen pressure of 0.8 MPa. The pressure was lowered to 0.7 MPa over 15 min, and the temperature inside the reaction vessel was increased to 75 $^\circ\text{C}$. When hydrogen uptake ceased, the catalyst was filtered off, and the filtrate was allowed to cool and stand until the two liquid phases completely separated. After removing the aqueous phase, the organic phase was evaporated to dryness, giving a solid (20 g) containing 2,2'-dichlorohydrazobenzene (87–92 wt%), *o*-chloroaniline (5–10 wt%), and 2-chlorohydrazobenzene (1.1–1.4 wt%). Recrystallization from anhydrous ethanol (100 ml) gave 2,2'-dichlorohydrazobenzene (17 g, 99%) as white crystals having mp 86–87 $^\circ\text{C}$ (lit. [21] mp 86–87 $^\circ\text{C}$). ^1H NMR (400 MHz, CDCl_3): δ 6.67–6.70 (m, 2H), δ 6.82–6.84 (d, 2H), δ 7.05–7.09 (m, 2H), δ 7.25–7.27 (d, 2H), δ 7.40–7.46 (d, 2H); ^{13}C NMR (100 MHz, CDCl_3) (δ): 112.5, 116.6, 118.7, 127.5, 128.9, 144.5.



Scheme 1. Diagram of process used to prepare modified Pd/C catalysts.

3. Results and discussion

3.1. Preparation and characterization of modified Pd/C

The surfactant molecules usually act as a “morphology-tunable” reagent for the preparation of inorganic nanocrystals in microemulsion. It has been noted that the growth of the nanocrystals depends strongly upon surfactant injection concentration. Our Cerium oxide (CeO_2) and iron oxide (Fe_2O_3) nanoparticles formed in the micropools of water (reverse micelles) in organic solvent. A layer of anionic

surfactants (cetylsulfonylacetic acid) capping the surface of nanocluster protected the nanosystem from aggregation and makes the particle dissolvable in toluene. Fig. 1 is TEM image of cerium oxide (CeO_2) and iron oxide (Fe_2O_3) nanoparticles, in which the particle size is about 1–2 nm with a narrow size distribution.

CeO_2 and Fe_2O_3 nanoparticles were capped with cetylsulfonylacetic acid, bonded to activated carbon (prepared by the submerging method [22]) in tetralin, and stirred under reflux until decarboxylation was complete. A schematic diagram for this process is given in Scheme 1. Figs. 2 and 3 show a representative TEM

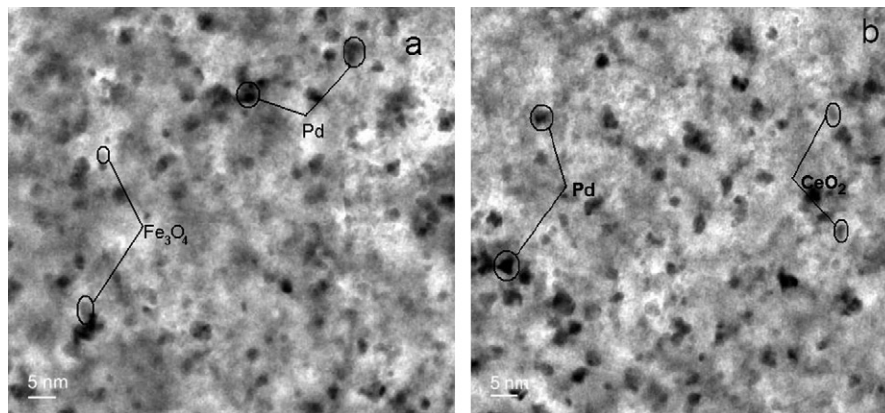


Fig. 2. TEM image of Pd/C catalyst doped with (a) Fe_3O_4 and (b) CeO_2 particles.

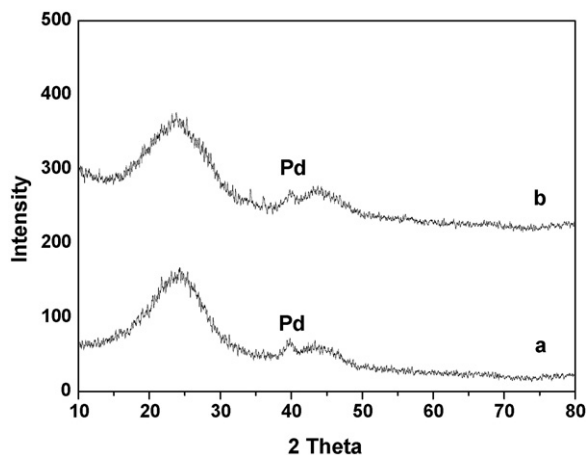


Fig. 3. XRD pattern of Pd/C catalyst doped with (a) Fe_3O_4 and (b) CeO_2 particles.

image and XRD pattern of Pd/C catalyst doped with cerium oxide particles. Fig. 2 shows that all Pd (black spots) or cerium oxide particles (gray spots) are well within nanosize, and it is clear that Pd and CeO_2 particles or Fe_2O_3 nanoparticles are commingled. Fig. 3 shows that Pd/C catalysts doped with CeO_2 or Fe_2O_3 particles exhibit a weak reflection peak, indicating that the Pd/ CeO_2 and Pd/ Fe_2O_3 matrix are essentially amorphous.

Carbon has been reported to be a better support for promoted Pd catalyst for the conversion of *o*-chloronitrobenzene to 2,2'-dichlorohydrazobenzene [7]. Carbon-doped CeO_2 and Fe_2O_3 nanoparticles possess the beneficial properties of both nanoparticles and carbon, like good form stability (due to interaction between nanoparticles and Pd) and reduction in Pd–Pd interaction (due to the presence of carbon covered with the nanoparticles). In view of the beneficial role of carbon coverage on CeO_2 and Fe_2O_3 nanoparticles, we performed a group of experiments to observe the variation of Pd/C catalyst in the conversion of *o*-chloronitrobenzene to 2,2'-dichlorohydrazobenzene. The corresponding TEM image and XRD pattern of the used Pd/C catalyst are shown in Figs. 4 and 5. Because of CeO_2 and Fe_2O_3 nanoparticles on the activated carbon support, the TEM image expresses few transformations on the Pd particles, which could be concluded the influence of CeO_2 and Fe_2O_3 nanoparticles as a promoter.

Fig. 5 shows XRD patterns of the used Pd/C catalyst doped with (a) Fe_3O_4 and (b) CeO_2 particles. The peaks, which are assigned to Pd metal [19], are observed on the Pd/C catalyst. On the other hand,

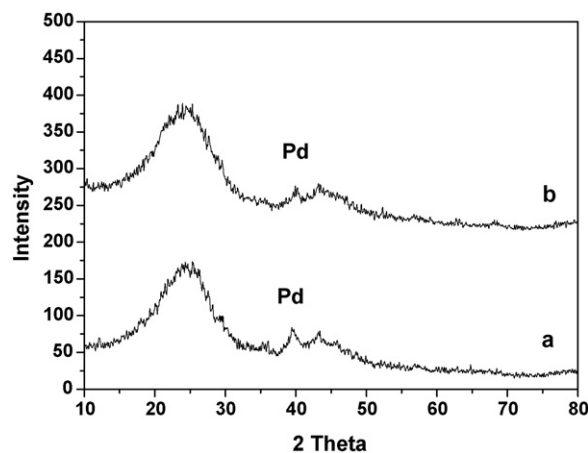


Fig. 5. XRD patterns of the used Pd/C catalyst modified with (a) Fe_3O_4 and (b) CeO_2 particles.

the peaks assigned Fe_3O_4 and CeO_2 are too weak to observe. XRD pattern (Fig. 4b) of the used Pd/C catalyst doped with CeO_2 particles shows a faintish signal to Pd, due to its high dispersion, which indicates the presence of Pd in small crystallites. Whereas in the used Pd/C catalyst doped with Fe_3O_4 particles, signal due to Pd is observed, indicating the formation of bigger Pd particles. However, in Pd/C catalyst, the influence of CeO_2 particles as a promoter, which plays major role in obtaining the high selectivity towards desired product to 2,2'-dichlorohydrazobenzene have been observed. This clearly indicates the advantage of incorporation of CeO_2 particles along with Pd to the carbon support. As TEM images show in Fig. 4, the mean particle size of the Pd on the used Pd/C catalysts doped with (a) Fe_3O_4 and (b) CeO_2 particles can be estimated to be 10 and 5.0 nm, respectively. Furthermore, from the comparison of XRD patterns and TEM images between the new Pd/C and the used Pd/C catalysts doped with Fe_3O_4 and CeO_2 particles, it is found that CeO_2 addition inhibits the aggregation of particles during hydrogen reduction.

3.2. Hydrogenation of *o*-chloronitrobenzene on modified Pd/C

The hydrogenation of *o*-chloronitrobenzene to give 2,2'-dichloroazoxybenzene was studied using HPLC, to determine the number and nature of the products. The catalytic hydrogenation of *o*-chloronitrobenzene a complex process consisting of

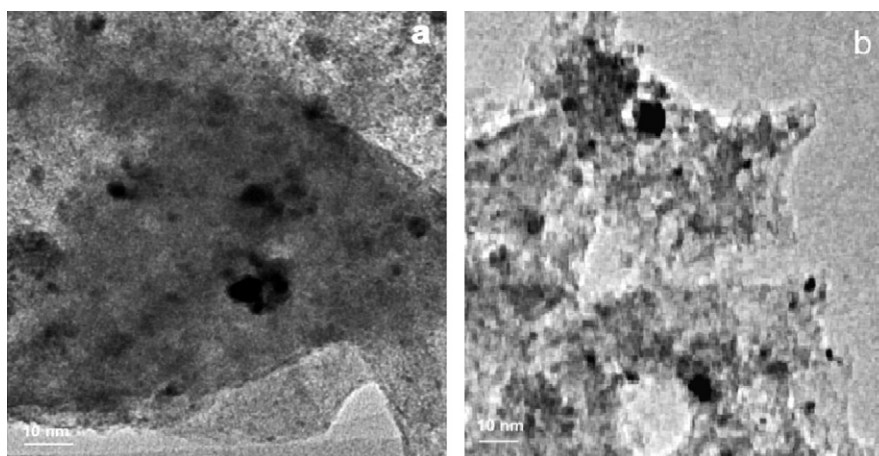
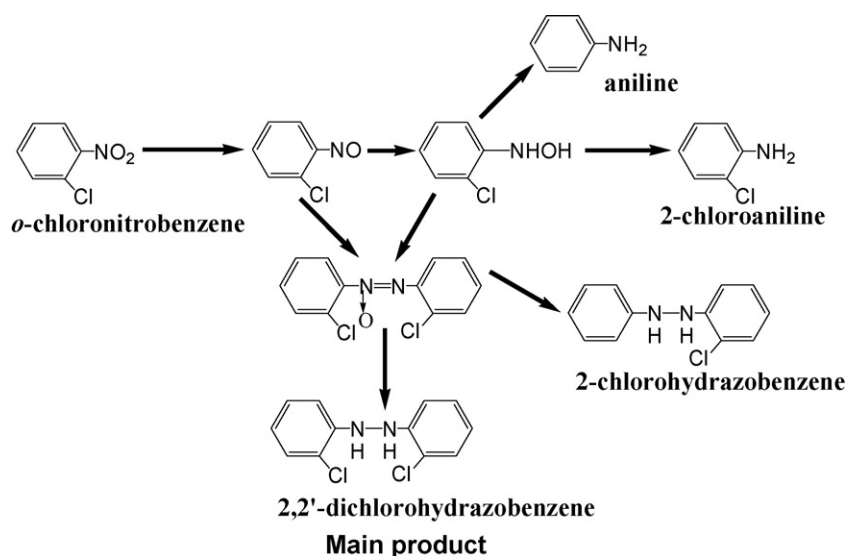


Fig. 4. TEM images of the used Pd/C catalyst modified with (a) Fe_3O_4 and (b) CeO_2 particles.



Scheme 2. Synthetic scheme for the formation of dichlorohydrazobenzene and key by-products.

four phases, viz., gaseous (H_2), organic (*o*-chloronitrobenzene), aqueous (NaOH solution), and solid (Pd/C). The catalyst plays a critical role in this process, as the reaction takes place at its active sites. The hydrogenation of *o*-chloronitrobenzene to give 2,2'-dichlorohydrazobenzene can be divided into two stages. During the first stage, the major reaction is the conversion of *o*-chloronitrobenzene to 2,2'-dichloroazoxybenzene, which is transformed mainly to 2,2'-dichlorohydrazobenzene during the second stage (Scheme 2). 2-Chloroaniline, aniline, and 2-chlorohydrazoxybenzene are by-products that must be controlled in order to have a viable process.

Tables 1 and 2 show results from the use of 1% Pd/C catalyst doped with Ce and Fe nanoparticles. From these tables it can be seen that the yield of 2,2'-dichlorohydrazoxybenzene was essentially the same as the Ce or Fe levels were varied from 0.5 to 3% and that the conversion of *o*-chloronitrobenzene to aniline and *o*-chloroaniline was about the same at different Ce and Fe levels. The results in Table 3 indicate that the hydrogenation process can be conducted at 55 °C rather than the previously reported 75 °C [7]. In comparison with unmodified 1% Pd/C catalyst, the yield of 2,2'-dichlorohydrazobenzene is essentially the same but the reaction time is shorter. It appears that the presence of nanosized metal oxides on the Pd/C catalyst enhances the surface available for the reduction process.

To study the stability of Pd/C modified with metal oxide particles, the hydrogenation was repeated with previously used catalyst, the results of which are shown in Tables 3 and 4. In these experiments, *o*-chloronitrobenzene and 1% modified Pd/C catalyst were used. Interestingly, increasing the reaction time as the number of repetitions increased pushed the yield of 2,2'-dichlorohydrazobenzene to 92%, and decreased the levels of *o*-chloroaniline and aniline. However, the amount of 2-chlorohydrazobenzene produced was essentially constant (~1.2%). Using unmodified Pd/C catalyst, results from our previous investigation show that the activity of this catalyst reduced dramatically as the numbers of repetitions increased and a certain amount of fresh catalyst was required to achieve the desired hydrogenation [7]. It was investigated that unmodified 0.8% Pd/C catalyst has a better capacity and provides better stability than unmodified 5% Pd/C with higher conversion to 2,2'-dichlorohydrazobenzene and lower conversion to *o*-chloroaniline (see Table 5).

From the present experimental results, it is clear that Pd/C modification using CeO_2 particles afforded better stability than the case involving modification with Fe_2O_3 . Using Ce-modified Pd/C catalyst, the reduction could be repeated up to four times without adversely affecting the conversion of *o*-chloronitrobenzene to the target product. However, the properties of Pd/C catalyst doped with Fe_2O_3 were adversely affected after two repetitions. These results

Table 1
Results from the reduction of *o*-chloronitrobenzene at 55 °C using 1% Pd/C containing various Ce levels

Expt. No.	Ce in Pd/C (%)	Reaction time (h)	2,2'-Dichlorohydrazobenzene (%)	2-Chlorohydrazobenzene (%)	<i>o</i> -Chloroaniline (%)	Aniline (%)
1	0.5	6.2	87.1	1.1	9.6	1.8
2	1.1	6.2	87.3	1.1	9.6	1.6
3	1.6	6.1	88.7	1.1	8.5	1.7
4	2.1	6.1	87.3	1.2	8.6	1.6
5	2.6	6.9	87.6	1.2	8.4	1.6
6	3.2	7.5	87.9	1.2	9.2	1.3

Table 2
Results from the reduction of *o*-chloronitrobenzene at 55 °C using 1% Pd/C containing various Fe levels

No.	Fe in Pd/C (%)	Reaction time (h)	2,2'-Dichlorohydrazobenzene (%)	2-Chlorohydrazobenzene (%)	<i>o</i> -Chloroaniline (%)	Aniline (%)
1	0.5	7.9	87.1	1.2	9.8	0.4
2	1.0	8.0	88.6	1.1	9.4	0.4
3	1.5	8.6	87.0	1.2	10.8	0.6
4	3.0	9.2	87.4	1.4	10.1	0.6

Table 3Results from the reduction of *o*-chloronitrobenzene using 1% Pd/C containing 1.6% Ce.

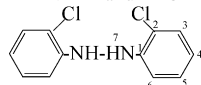
No. of repeats	Reaction time (h)		2,2'-Dichlorohydrazobenzene (%)	2-Chlorohydrazobenzene (%)	<i>o</i> -Chloroaniline (%)	Aniline (%)
	55 °C	75 °C				
0	6.1	0	88.7	1.1	8.5	1.7
1	6.3	0	90.2	1.0	7.7	1.0
2	7.3	0	91.6	1.3	6.1	0.8
3	15.7	0	92.1	1.0	5.6	0.6
4	4.9	10.7	92.4	1.2	5.2	0.5

Table 4Results from the reduction of *o*-chloronitrobenzene using 1% Pd/C containing 1.5% Fe

No. of repeats	Reaction time (h)		2,2'-Dichlorohydrazobenzene (%)	2-Chlorohydrazobenzene (%)	<i>o</i> -Chloroaniline (%)	Aniline (%)
	55 °C	75 °C				
0	8.6	0	87.0	1.2	10.8	0.6
1	11.6	0	90.3	1.0	7.6	0.2
2	14.5	1.6	92.0	1.3	5.7	0.1

Table 5Relative activities of 0.8% and 5% unmodified Pd/C catalyst catalysts for hydrogenating *o*-nitrochlorobenzene

Catalyst	No. of repeats	Reaction time (h)	2,2'-Dichlorohydrazobenzene (%)	<i>o</i> -Chloroaniline (%)	Aniline (%)
5% Pd/C	1 ^a	8	83.5	4.1	12.9
5% Pd/C	2 ^b	11.5	81.6	4.8	12.5
5% Pd/C	3	10	80.6	4.4	13.4
5% Pd/C	4	12	76.0	7.6	15.4
0.8% Pd/C	1 ^a	9	95.5	2.46	1.5
0.8% Pd/C	2 ^b	13	93.9	2.99	2.2
0.8% Pd/C	3	12.5	95.2	3.05	1.25
0.8% Pd/C	4	11.5	93.8	3.28	2.1

^a For newly prepared Pd/C catalysts, the rate of catalyst consumption per gram of *o*-nitrochlorobenzene comprised approximately 2% of that observed in the hydrogenation.^b From the second experiment, the used Pd/C catalyst and one fourth of new Pd/C catalyst were employed together on the hydrogenation of *o*-nitrochlorobenzene.**Table 6**¹H NMR and ¹³C NMR data for 2,2'-dichlorohydrazobenzene in CDCl₃

C/H no.	δ (ppm) (¹ H)	δ (ppm) (¹³ C)
1	–	144.5
2	–	116.6
3	7.25–7.27, 2H	128.9
4	6.67–6.70, 2H	118.7
5	7.05–7.09, 2H	127.5
6	6.82–6.84, 2H	112.5
7	7.40–7.46, 2H	–

are consistent with the work of others, in which it was reported that the use of CeO₂ as an additive improves the catalytic activity of certain noble metals, especially at metal/oxide interfaces [23,24].

When the hydrogenation of *o*-chloronitrobenzene was complete, pink crystals of 2,2'-dichlorohydrazobenzene were obtained, which became white after recrystallization from anhydrous ethanol. The chemical structure of the target compound was confirmed using ¹H and ¹³C NMR spectroscopy (Table 6). The expected number and types of signals for protons and carbons were observed. For instance, signals for proton H-4 and carbon C-1 were observed at δ 6.67–6.70 and 144.5, respectively.

4. Conclusions

Pd/C catalysts modified with CeO₂ and Fe₂O₃ nanoparticles using a new thermal decarboxylation method involving cetylsulfonyl acetate can be used for efficient conversion of *o*-chloronitrobenzene to 2,2'-dichlorohydrazobenzene. The presence

of the two metal oxides on Pd/C catalyst affected its activity and stability. In this regard, Pd/C catalyst doped with CeO₂ exhibited better stability than the Fe₂O₃-doped catalyst. Pd/C catalyst doped with the former could be reused up to five times without the need to add fresh catalyst and the yield of 2,2'-dichlorohydrazobenzene was as high as 92%.

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