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Synthesis of carbon-supported Pd/SnO_2 catalyst for highly selective hydrogenation of 2,4-difluoronitrobenzene

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ABSTRACT

Halogenated anilines have a wide range of applications in the production of pharmaceuticals and agrochemical substances, and thus it is of great importance to develop highly active and selective catalysts for the hydrogenation of halogenated nitrobenzenes. We approach this challenge by probing noble metal/non-noble metal oxide nanoparticles (NPs) catalysts. Carbon-supported Pd/SnO_2 catalysts were synthesized by the chemical reduction method, and their catalytic activity was evaluated by the hydrogenation reaction of 2,4-difluoronitrobenzene (DFNB) to the corresponding 2,4-difluoroaniline (DFAN), showing a remarkable synergistic effect of the Pd and SnO_2 NPs. The as-prepared $Pd/SnO_2/C$ catalysts were characterized using TEM, XRD, H_2 TPD and XPS techniques. Modifications to the electronic structure of the Pd atoms through the use of SnO_2 led to the suppression of the hydrogenolysis of the C–F bond and the acceleration of nitrosobenzene (DFNSB) conversion and consequently, resulted in the inhibition of the formation of reactive by-products and may be responsible for the enhancements observed in selectivity.

1. Introduction

Functionalized anilines are important intermediates for pharmaceuticals, polymers, herbicides, and other substances and fine chemicals. Among them, fluoroanilines (FA) are important building blocks for the synthesis of numerous bioactive products [1–4]. For their importance, the selective hydrogenation of aromatic nitro compounds to the corresponding anilines is an industrially important reaction [5–9].

A broad range of catalysts for the hydrogenation of halogenated nitrobenzenes has been well-studied, such as Pt [5], Pd [6], Rh [7] and Ni [10] catalysts. Depending on the halogens and their position relative to the nitro group in the halogenated nitrobenzene, hydrogenolysis of the C–X bond and nucleophilic substitution of the C–N coupling reaction leading to the formation of nitro- and/or amino-diphenylamine, may happen varying from negligible to 100% [11,12]. Great efforts have been made to improve the hydrogenation selectivity, such as choosing efficient supports [13–15], adding promoters [16,17], poisoning [18] and alloying [19]. However, on one hand, catalysts such as Pd/C with high intrinsic activity suffer from low selectivity. On the other hand, catalysts of higher selectivity obtained by poisoning or alloying require high reaction temperature and high H_2 pressure because of their lower intrinsic activity. Recently, more and more attention has been focused on the noble metal/non-noble metal oxide NPs catalysts as potential catalysts for the hydrogenation of halogenated nitrobenzenes. These catalysts often display a higher performance than their monometallic counterparts. In Coq's study [20], the catalytic hydrogenation properties of Pt/TiO_2 and Pt/Al_2O_3 catalysts using *p*-chloronitrobenzene (*p*-CNB) as a model substrate were compared and it was found that the ratio of the hydrogenation activity to hydrodechlorination activity over the Pt/TiO_2 catalyst was 10-fold higher than that over the Pt/Al_2O_3 catalyst. More recently, Wang [21] reported that the assembled Ru/SnO_2 catalysts exhibited excellent catalytic activity in the hydrogenation of *o*-chloronitrobenzene (*o*-CNB) to the corresponding *o*-chloroaniline (*o*-CAN), and the catalytic activity surpassed that of all previously reported Ru catalysts. And the selectivity of the *o*-CAN was in agreement with the best results reported on a colloidal Ru catalyst so far. Notably, the non-noble metal oxide appears necessary to provide a desired chemical interface between the NPs and the reaction media. Herein, the catalytic activity of $Pd/SnO_2/C$ catalysts was investigated for the liquid-phase hydrogenation of 2,4-difluoronitrobenzene (DFNB) to 2,4-difluoroaniline (DFAN) under mild reaction conditions, and some new insights about the catalytic properties of $Pd/SnO_2/C$ were revealed.

2. Experimental

The $Pd/SnO_2/C$ catalysts were prepared in two steps: first deposition of the SnO_2 onto the carbon followed by the deposition of Pd. Bu_3SnCl was then charged into an aqueous slurry of the

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carbon support to obtain a SnO_2 loading of 10 wt%, then the pH value was adjusted to 8–9 under stirring. Subsequently, the solid was collected by filtration, washed, dried and then calcined in N_2 gas stream at 773 K for 4 h. Then an aqueous solution of H_2PdCl_4 (0.05 g_{metal}/mL) was added into an aqueous slurry of the SnO_2/C supports to obtain a Pd loading of 2 wt%. After stirring, the solution pH value of 8–9 was reached, then the precipitated $Pd(OH)_2$ was reduced by hydrazine hydrate. Finally, the slurry was washed and dried under vacuum at 383 K for 10 h, and kept for use. The Pd/C heterogeneous catalyst with 2 wt% Pd loading was also prepared using the same procedures. A classical Pd/SnO_2 heterogeneous catalyst with 2 wt% Pd loading was also prepared by the traditional wetness impregnation method using H_2PdCl_4 and prepared SnO_2 supports as precursors. The SnO_2 support was prepared by neutralizing the prepared SnO_2 sol with an aqueous solution of NaOH and drying the SnO_2 precipitate at 383 K. The catalyst was calcined at 573 K for 2 h and reduced with hydrogen at 523 K for 3 h.

TEM study was carried out in a Philips-FEI Tecnai G2 F30 S-Twin instrument. XRD measurements of the catalyst samples were performed on a PANalytical-X'Pert PRO generator. XPS was acquired with a Kratos AXIS Ultra DLD spectrometer. H_2 TPD experiments were performed by first reducing the sample *in situ* at 200 °C. Then the sample was swept with pure Ar to remove physiosorbed and/or weakly bound species. The TPD spectra were recorded by TCD.

Liquid phase hydrogenation of DFNB was conducted as follows: 150 mL of ethanol, 10.0 g of DFNB, and 0.1 g of the catalyst were mixed in a 500-mL steel autoclave. Air in the autoclave was purged by hydrogen, and then the reaction proceeded at the required temperature (363 K) and at 1 MPa of 99.99% pure hydrogen. The selectivity of the hydrogenation of DFNB was calculated using the following equations:

$$\text{Selectivity}_{\text{DFAN}} = \frac{m_{\text{DFAN}}\%}{m_{\text{DFAN}}\% + m_{\text{2-FAN}}\% + m_{\text{4-FAN}}\% + m_{\text{AN}}\% + m_{\text{OBP}}\%} \times 100\%$$

where 2-FAN represents 2-fluoroaniline; 4-FAN represents 4-fluoroaniline; AN represents aniline; OBP represents the amount of azoxybenzene (AOB), azobenzene (AB), hydrazobenzene (HAB), *N*-phenylhydroxylamine (PHA), nitrosobenzene (NSB), aminodiphenylamine (ADPA) and nitrodiphenylamine (NDPA) in the mixture.

3. Results and discussion

Fig. 1a showed that the Pd NPs were highly dispersed on the SnO_2 NPs. As indicated in Fig. 1b, there were two kinds of lattice planes that were identified with the NPs, which correspond to the (1 1 0) plane of SnO_2 and the (2 0 0) plane of Pd. Generally, the activation energy for heterogeneous nucleation is lower than that for homogeneous nucleation [22], which results in Pd^0 atoms depositing on SnO_2 surfaces rather than forming discrete Pd NPs on carbon support. The size of Pd particles was distributed mainly in the range of 3–5 nm with an average size of Pd NPs being about 4 nm (Fig. 1a). In the XRD patterns shown in Fig. 2, the obvious crystal planes of the SnO_2 were observed for both SnO_2/C and Pd/SnO_2/C samples. The peaks corresponding to Pd NPs at $2\theta = 40.13°$ and 46.96° relative to the (1 1 1) and (2 2 0) planes, respectively, could be observed (Fig. 2b). As shown in Fig. 3, the areas of the H_2 TPD peaks for the Pd/SnO_2/C catalyst were much larger than those for the Pd/C and Pd/SnO_2 catalysts, which may be attributed to the hydrogen spillover effect in Pd/SnO_2/C. The enhancement in the amount of chemosorbed hydrogen may be beneficial for improving catalytic activity [23]. The XPS core level spectra of Pd 3d of the various catalysts are shown in Fig. 4. The Pd 3d peaks were detected at a range of binding energy (BE) of 335.1–335.5 eV for the Pd/C, Pd/SnO_2 and Pd/SnO_2/C catalysts, which is typical for metallic Pd^0 [24]. In addition, the binding energy of Pd $3d_{5/2}$ detected at 336.5–337.1 eV was attributed to the presence of palladium in the form of $Pd^{II}O$. The presence of $Pd^{II}O$ on the surface was ascribed to the easy oxidation of Pd upon contact with air at room temperature. It was observed that in the Pd/SnO_2 and Pd/SnO_2/C samples, the position of the Pd^0 $3d_{5/2}$ signal presented a slightly shift of 0.3 eV and 0.4 eV, respectively, compared with that of the Pd/C sample, which presented at a binding energy of 335.1 eV. Upon the addition of the SnO_2, the electronic structure of the surface Pd atoms was modified.

When the hydrogenation of nitrobenzene was carried out in organic solvents, several intermediates were frequently produced and accumulated during the reaction [25–29]. In the case of fluoronitrobenzene, a possible side reaction is the nucleophilic substitution C–N coupling reaction that leads to the formation of amino- and/or nitro-diphenylamine. Interestingly, the production of these intermediates was inhibited when hydrogenation of nitrobenzene was catalyzed using a Pd/SnO_2/C catalyst, and the results can be found in Table 1. Throughout the whole reaction process, 100% DFAN selectivity was achieved and no undesired

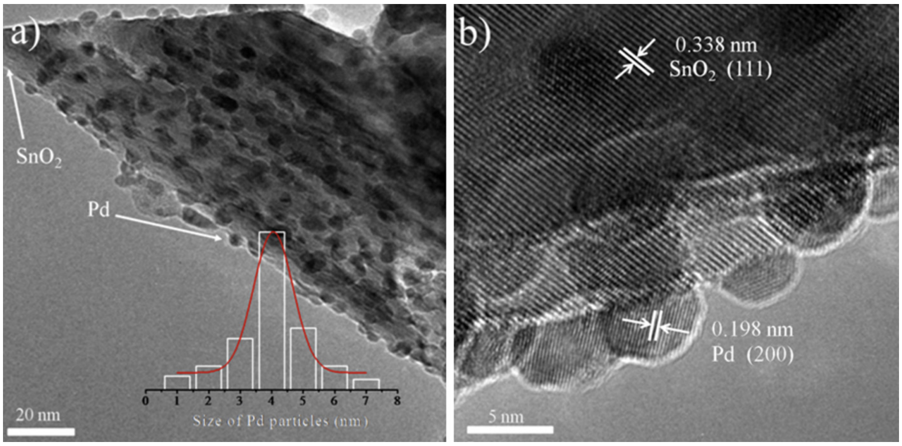

Fig. 1. (a) TEM image of Pd/SnO_2/C and the crystallite size distribution and (b) HRTEM image of Pd/SnO_2/C.

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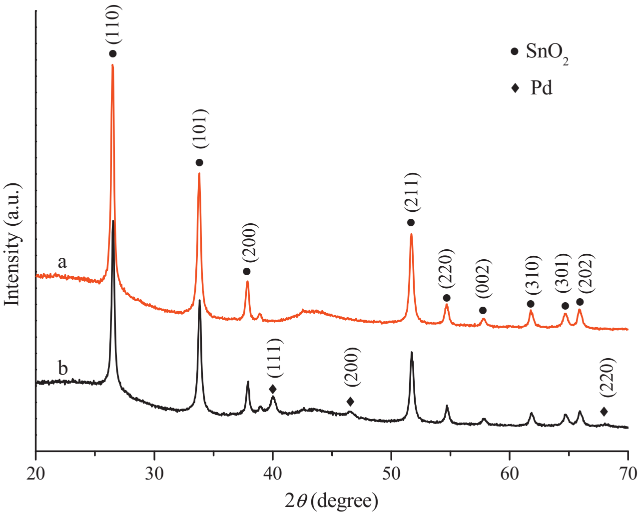

Fig. 2. XRD patterns of (a) SnO_2/C and (b) Pd/SnO_2/C.

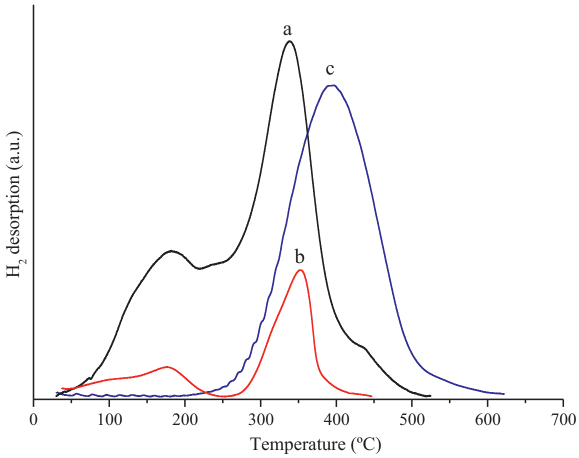

Fig. 3. H_2 TPD profiles of (a) Pd/SnO_2/C, (b) Pd/SnO_2, and (c) Pd/C.

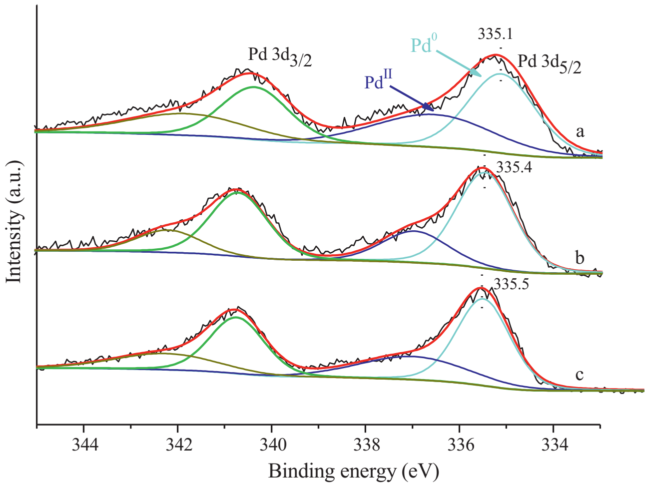

Fig. 4. Pd 3d photoemission core-level spectra for (a) Pd/C, (b) Pd/SnO_2 and (c) Pd/SnO_2/C.

Table 1
Catalytic results of the hydrogenation of DFNB.[a]

	Catalysts			
	Pd/C	Pd/SnO_2	Pd/SnO_2/C	SnO_2/C
Selectivity (%)[b]	96.47	99.96	100	–
Reaction rate[c]	1.99	0.84	3.72	–
Conversion (%)	100	100	100	–

[a] Reaction conditions: 0.1 g catalyst; 20.0 g 2,4-difluoronitrobenzene; 150 mL ethanol; P_{H_2} = 1.0 MPa; T = 353 K; stirring rate = 1000 rpm.

[b] Only ADPA and NDPA be detected among all by-products in the mixture under the conditions.

[c] Reaction rate unit: mol-substrates/mol-Pd s.

intermediates accumulated during the reaction. For the Pd/C, the selectivity of DFAN was only 96.47%. In addition, the carbon supported Pd/SnO_2 catalyst exhibited unexpected activity. Although the high selectivity of DFAN (99.96%) was also achieved on the Pd/SnO_2 catalyst, the catalytic activity decreased remarkably. The Pd/SnO_2 catalyst presented a lower activity in converting DFNB when compared with the Pd/SnO_2/C catalyst, which might be attributed to the fact that the latter possessed more accessible surface areas. Using the SnO_2/C catalysts, the hydrogenation reaction could not proceed because of the absence of the sites activating hydrogen.

The stability of Pd/SnO_2/C was also examined; the catalysts were reused directly without any treatment after precipitated and separated from the reaction solution. It was noted that the catalysts should be immersed in the solution during the recycling process to avoid the oxidation of the active Pd species. The Pd/SnO_2/C presented as relatively stable under the reaction conditions. Although the activity decreased slightly, there is no significant decrease in selectivity for at least 5 cycles (Fig. 5).

Coq [20] has reported that modulating the interactions between metal particles and supports could improve the selectivity, and proposed that suboxide TiO_x species migrating on the Pt particles could polarize the NO bond in *p*-CNB and would then be responsible for promoting the hydrogenation activity. With respect to the effect of SnO_2 as a support of Pd, it can be suggested that in our case the effect of SnO_2 is related to the acidity of the Sn ions (Lewis acidity), which activate the NO group by enhancing its positive charge. Another positive effect could also result from the formation of the electron-donor levels (oxygen vacancies V^0) or the increase of coordinatively unsaturated Sn^{2+} or Sn^{4+} species at the surface of SnO_2 in a reducing atmosphere such as H_2 [30], which would increase the free electron concentration. These unsaturated Sn^{2+} or Sn^{4+} surface species support the Pd NPs, may activate the

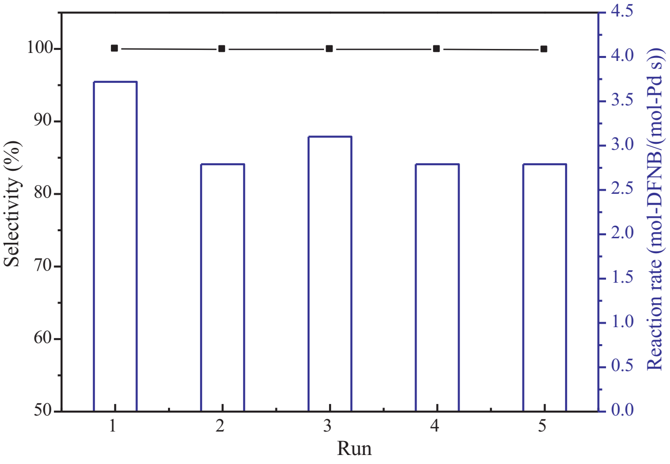

Fig. 5. The recycling results for Pd/SnO_2/C catalyst in the hydrogenation of DFNB.

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polar NO groups of DFNB and coordinate with the NH_2 groups of DFAN, thereby promote the hydrogenation of DFNB and suppress both the hydrodehalorination and coupling side reactions. Combining the XPS and H_2 TPD analysis, the significantly improved catalytic activity of Pd/SnO_2/C catalysts was likely resulted from the enhancement in the amount of active species and the strong interactions between Pd and SnO_2 NPs, which lead to the high activity of Pd active species. However, it should be noted that a slight binding energy shift of 0.4 eV on the Pd^0 $3d_{5/2}$ peak could be detected, which strongly indicates an electron transfer from Pd to SnO_2 due to its strong electron withdrawing ability, which may suppress the hydrogenolysis of C–F bond.

4. Conclusion

The prepared Pd/SnO_2/C catalyst displays a high performance (selectivity, activity and stability) for the hydrogenation of DFNB to the corresponding DFAN. The enhance performance may partially be derived from the coordination action between the NH_2 groups and coordinatively unsaturated Sn^{2+} or Sn^{4+} species at the surface of SnO_2 to form Pd–Sn^{n+} ion pairs. These oxygen vacancies of SnO_2 produced under reductive atmosphere are believed to account for the high catalytic activity and selectivity in the hydrogenation of DFNB. In addition, the upward shift of Pd^0 binding energy indicates an electron deficiency of Pd due to an electron transfer from Pd to SnO_2, which may suppress the hydrogenolysis of C–F bonds. The excellent catalytic performance and good recyclability of the Pd/SnO_2/C catalyst will make it attractive for fundamental research and practical applications.

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