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Short communication

Nitrogen doped carbon supported iron catalysts for highly selective production of 4,4'-diamino-2,2'-stilbenedisulfonic acid



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ARTICLE INFO	A B S T R A C T
Keywords:	Nitrogen doped carbon supported iron catalysts were prepared from pyrolysis of a multidentate nitrogen ligand
Iron nanoparticles	iron complex supported on chitosan at different temperature, and showed good performances in the reduction of
Nitrogen doped carbon	4,4'-dinitrostilbene-2,2'-disulfonic acid (DNS acid) to 4,4'-diamino-2,2'-stilbenedisulfonic acid (DSD acid) with
DSD acid DNS acid Hydrazine hydrate	hydrazine hydrate (N_2H_4 · H_2O) as reductant. Characterization results revealed that the iron is mainly present in the form of Fe ₂ O ₃ and metallic iron nanoparticles. The doped N atoms functionalized as anchoring sites to stabilize iron nanoparticles, which endows the catalysts with excellent activity and superior reusability.

1. Introduction

4,4'-Diamino-2,2'-stilbenedisulfonic acid (DSD acid) is an important intermediate widely used for manufacturing dyes, pigments and fluorescent brightener [1-5]. Now, DSD acid is mainly produced from iron powder reduction of 4,4'-dinitrostilbene-2,2'-disulfonic acid (DNS acid) in China [1,2]. The reduction of DNS acid with iron powder can tolerate co-existence of C=C double bond in the structure affording DSD acid with high selectivity, but generate large amount of iron mud harmful to environment. Therefore, efforts were made to develop alternative protocols to prepare DSD acid, such as electrochemical reduction [6] and catalytic reduction of DNS acid using various reductants [2,7]. The electrochemical reduction protocol encountered the bottleneck of low current efficiency [6]. In 2012, Chen et al. reported the preparation and the catalysis of gold nanoparticles supported on three metal oxides for the reduction of DNS acid to DSD acid with H₂, CO and HCO₂Na as reductants [2]. A selectivity higher than 94% was achieved over the three Au NPs containing catalysts. However, the high cost of noble metal based catalysts will become a big obstacle for the manufacture of DSD acid belonging to a less expensive product.

It is well known that hydrazine hydrate $(N_2H_4H_2O)$ is a good hydrogen source for the reduction of nitro compounds to amines over iron based catalysts [8–10], [14–16]. In principle, only nitrogen and water are the byproducts in the reduction of nitro compounds with N_2H_4 ·H₂O. On the other hand, iron is non-toxic, cheap, and easily available.

Therefore, it is promising to develop an efficient and sustainable iron based catalyst for the conversion of DNS acid to DSD acid using $N_2H_4{\cdot}H_2O$ as reductant.

Recently, nitrogen doped carbon supported metal catalysts have attracted much attention due to their excellent activity and selectivity in the reduction of nitro compounds with various hydrogen sources [11–23]. The doped nitrogen could facilitate the transfer hydrogenation of nitro compounds, due to the synergistic effect between the doped nitrogen and the metal species in the catalysts as revealed by Beller [15,16]. Beller [15] also found that the performance of a catalyst could be controlled by the ligand in the complex and the support in the preparation of the heterogeneous catalyst. The nitrogen numbers coordinated to center metal in a complex is of great importance to give highly active species in the prepared catalyst. Meanwhile, a suitable match of a complex with a support is also important to afford a catalyst with good performance.

Herein, nitrogen doped carbon supported iron catalysts (FeNC-T, T = 700, 800, 900 °C) were prepared through pyrolysis a multidentate nitrogen ligand iron complex Fe(phen)(pydic) absorbed on chitosan at different temperature, and applied to the reduction of DNS acid to DSD acid with N₂H₄·H₂O. N₂H₄·H₂O functionalized as hydrogen source endows this strategy a green route to synthesis DSD acid. Characterization results revealed that iron species mainly exist in the form of Fe₂O₃ and metallic iron nanoparticles and anchor on the doped nitrogen atoms, thus affording the catalysts good performances in application.

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Fig. 1. (a) XRD patterns (b) XPS survey scan, (c) high resolution XPS analysis in N 1s region, and (d) detailed Fe 2p spectra of catalyst samples.

2. Experimental

The experimental procedures were given in Supplementary information.

3. Results and discussion

3.1. Catalyst characterization

XRD and XPS were performed to disclose the compositions and valence states of as prepared catalysts. As shown in Fig. 1a, diffraction peak located at 20 of 26[°] is assigned to graphitic carbon [24], the ones at 20 of 35.6[°], 44.7[°] are assigned to Fe₂O₃ [25,26] and metallic iron [13,25,27], respectively. It is also found that with the pyrolysis temperature raised to 900 °C, diffraction peaks of Fe₃C is observed in the 20 range of 40 to 50[°], indicating partial transformation of metallic iron into Fe₃C [27]. Pyrolysis at high temperature of an iron and carbon-containing material led to reduction of iron species to metallic iron by carbon, and the metallic iron was chemically extremely active to react with other atoms such nitrogen and carbon to form FeN_x or FeC_x species [27].

XPS survey scan spectra are shown in Fig. 1b, the signals of C, N, and Fe are observed in the spectra of all the three samples. It is found that the content of nitrogen decreases with the increase of pyrolysis temperature, which is in consistent with elemental analysis (Table S1). Careful deconvolution of N 1s spectra (Fig. 1c) reveals that surface nitrogen species exist in the forms of graphitic N (401.3 eV), pyrrolic N (400.4 eV), Fe-Nx N(399.3 eV) and pyridinic N (398.7 eV) [27,28]. The contents of the four nitrogen species and the total nitrogen content in the three catalysts were determined by XPS, and the results are listed in Table S2. The total nitrogen content in the catalysts decreased with increase of pyrolysis temperature in the preparation of catalysts. Though the total nitrogen content in FeNC-800 is lower than that in FeNC-700, the nitrogen content of Fe-N_x N in FeNC-800 (0.65%) is higher than the ones in FeNC-700 (0.58%) and FeNC-900 (0.48%). Deconvolution of Fe 2p spectra reveals peaks at the binding energies of 710.0 eV, 712.8 eV, 716.5 eV. The peak at 710.0 eV is ascribed to the binding energy $2p_{3/2}$ of Fe(III) species [29,30] The peak at 716.5 eV has been identified as a satellite peak corresponding to Fe $2p_{3/2}$ [31]. The peak at 712.8 is attributed to FeN_x $2p_{3/2}$ [30] while the peaks at 723.2 eV and 725.7 eV are attributed to the binding energies $2p_{1/2}$ of Fe₂O₃ and FeN_x $2p_{1/2}$ [30].

(Fig. 1d). The separation of Fe (III) $2p_{3/2}$ and Fe (III) $2p_{1/2}$ is 13.2 eV, indicating the existence of Fe₂O₃ in the catalysts [13]. Combined with the fitted N 1s XPS spectrum, we can conclude that partial Fe species exist in the form of FeN_x, which means iron coordinating with doped nitrogen.

The morphologies and microstructures of catalyst FeNC-800 were revealed by TEM. As shown in Fig. S1, the iron nanoparticles show a homogeneous dispersion. Corresponding element mapping images indicate a homogeneous dispersion of element C, N, and same location area of FeN_x and Fe₂O₃. The element mapping images in combination with XPS analysis indicate that Fe₂O₃ species rooted in the FeN_x species to form iron nanoparticles, which is of great importance in determining the catalysis of the catalysts due to synergistic effect between iron nanoparticles and nitrogen doped carbon support [32,33].

 N_2 adsorption-desorption analysis revealed that all catalysts display type-IV isotherms (Fig. S2), indicating the presence of mesoporous pores in the catalysts. As shown in Table S3, catalyst FeNC-800 has the largest specific areas of 125.34 m² g⁻¹. Pyrolysis at temperature either higher or lower than 800 °C would lead to decrease of specific areas of the catalysts. Larger specific areas will endow more active species exposing to reactants in catalytic run. Therefore, FeNC-800 will show good performance compared to the other ones in the reductive conversion of DNS acid to DSD acid with N_2H_4 ·H₂O.

3.2. Catalytic performance

Preliminary experiments indicated that catalyst FeNC-800 gave best results in the reduction of DNS acid to DSD acid with N_2H_4 · H_2O in water among the three FeNC-T catalysts. Therefore, the effects of various parameters including reaction temperature, amount of N_2H_4 · H_2O and catalyst loading on the catalysis of FeNC-800 were investigated in water by maintaining reaction time 5 h, and the results are given in

Table 1

Catalytic performances of different catalysts.

Entry	Catalyst	Conversion (%) ^a	Selectivity (%) ^a
1	FeNC-700	99.8	83.1
2	FeNC-800	99.9	84.1
3	FeNC-900	99.9	78.6
4	NC-800	59.8	-
5 ^b	FeCl ₃ /AC	99.9	45.0
2 3 4 5 ^b	FeNC-800 FeNC-900 NC-800 FeCl ₃ /AC	99.9 99.9 59.8 99.9	84.1 78.6 - 45.0

Reaction conditions: DNS acid 0.5 mmol, methanol 2 mL, water 3 mL, hydrazine hydrate 2.25 mmol, catalyst 50 mg (7 mol% Fe), reaction temperature 140 °C, 1 bar $\rm N_2,$ reaction time 5 h.

 $^{\rm a}$ Conversion and selectivity were determined by HPLC external standard method.

 $^{\rm b}~$ FeCl_3 15 mg, AC 30 mg, methanol 10 mL, DNS 0.5 mmol, hydrazine hydrate 2 mmol, reflux temperature, 5 h,1 bar $\rm N_2.$

supplementary information (Table S4a–c). The suitable reaction temperature, amount of N₂H₄·H₂O and catalyst loading were determined to be 140 °C, 4.5 equivalents N₂H₄·H₂O to DNS acid and 7 mol%, respectively. In this case the conversion of DNS acid reached close to100%, with 80.3% selectivity of DSD acid. Herein, intermediate 4-amino-4'-nitrodiphenylethylene-2,2'-disulfonic acid (ANSD acid), and some unidentified oligomers were found in the reaction mixture, which led to the decrease of the selectivity of DSD acid. No 4,4'-diaminobibenzyl-2,2'-disulfonic acid (DAD acid) was detected in the reaction, indicating that this protocol can tolerate co-existence of C=C double bond in DNS acid. DAD acid is generally generated from over hydrogenation of DSD acid in the hydrogenation of DNS acid to DSD acid, leading to decrease of the selectivity of DSD acid [2].

Efforts were made to improve the selectivity of DSD acid by performing the reaction in organic solvents, but failed due to its poor solubility of DNS acid in organic solvents. Thankfully, introduction of appropriate amount of methanol into water could improve the reaction in some degree (Table S5). Initially, the selectivity of DSD acid increased with the introduction of methanol, and reached its maximum of 83.1% at methanol to water volume ratio of 2:3. Instead, further increase of methanol content led to a decrease of the selectivity of DSD, probably due to the low solubility of DNS in methanol. Therefore, the suitable solvent is the mixture of methanol and water in volume ratio of 2:3. After the suitable solvent was gotten, the reaction time was evaluated and determined to be 5 h (Table S6).

Based on the above results, the optimized reaction conditions were obtained, which were reaction temperature 140 °C, catalyst loading 7 mol%, 4.5 equivalents N_2H_4 H₂O, methanol to water volume ratio of 2:3, and reaction time 5 h. In this case the yield of DSD acid reached 83.1%.

The catalysis of as prepared catalysts was compared under the optimized reaction conditions. As shown in Table 1, catalyst FeNC-800 showed best selectivity towards DSD acid, and catalyst FeNC-700 performed slight worse compared to catalyst FeNC-800, but better than catalyst FeNC-900. The selectivities of DSD acid over the three catalysts were in agreement with the Fe-N_x N contents in FeNC-700 (0.58%), FeNC-800 (0.65%) and FeNC-900 (0.49%). The higher the Fe-N_x N content in the catalyst is, the higher selectivity of DSD acid is. This can be ascribed to that the higher \mbox{FeN}_x N content will lead more $\mbox{Fe}_2\mbox{O}_3$ nanoparticles formed, rooting in FeN_x species. Fe_2O_3 nanoparticles rooting in Fe-N_x species can be confirmed by element mapping images (Fig. S1). Fe₂O₃ nanoparticles rooting in FeN_x species are active species in the reduction of DNS acid to DSD acid with N2H4:H2O. Therefore, the catalyst FeNC-800 performed best among the three catalysts. The largest specific areas of FeNC-800 might be another reason that FeNC-800 showed best performance in the reaction. Besides, the poor performance of FeNC-900 compared to FeNC-700 and FeNC-800 could be partially ascribed to the transformation of iron species into Fe₃C in FeNC-900.



Fig. 2. Recyclability of catalyst FeNC-800.

Instead of DSD acid, nitroso and hydroxylamine intermediates as main products were detected over iron-free material NC-800, indicating their necessity of iron species in the catalysts. It is known that ferric trichloride in combination with active carbon (FeCl₃/AC) was very active in the reduction of nitro compounds with N₂H₄·H₂O [34]. Therefore, the reaction was also carried out with FeCl₃/AC as catalyst. Though the conversion of DNS acid was near 100% in the presence of FeCl₃/AC, the selectivity towards DSD acid was only 45%. The results in combination with the catalytic results of FeNC-800 indicated the great importance of the texture properties of FeNC-800, and presence of synergistic effect between iron nanoparticles and nitrogen doped carbon support in FeNC-800.

Finally, the reusability of FeNC-800 was examined for three recycles (Fig. 2) and no obvious decrease in activity was found in the recycle runs, indicating the excellent stability and reusability of FeNC-800 catalyst.

4. Conclusion

In summary, nitrogen doped carbon supported iron nanoparticles were readily prepared through pyrolysis an iron complex Fe(phen) (pydic) absorbed on chitosan. In these materials, the iron nanoparticles anchor on the doped N atoms in the carbon matrix. These materials, especially FeNC-800, as catalysts exhibited high activity and selectivity in the reduction of DNS to DSD with N_2H_4 · H_2O , and had advantages of easy recovery and good reusability, endowing this strategy a green and sustainable route to synthesis DSD acid from DNS acid.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2019.105822.

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