

Graphene encapsulated low-load nitrogen-doped bimetallic magnetic Pd/Fe@N/C catalyst for the reductive amination of nitroarene under mild conditions

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ABSTRACT

Aniline is a group of important platform molecules and is widely used in the synthesis of other high-value chemicals and pharmaceutical products. How to produce high-value anilines as the high-value chemical intermediates more efficiently and more environmentally has always been a research topic in the industry. Catalytic hydrogenation is an environmentally friendly method for preparing halogenated anilines. Traditional noble metals catalysis face cost and noble metals residue problems. To improve the purity of the product and the activity and recyclability of the catalyst, we prepared a Pd/Fe magnetic bimetallic catalyst supported on N-doped carbon materials to reduce nitrobenzene to aniline under mild conditions. The loading of Pd was very low, which was 1/10 of the content of common commercial precious metal Pd/C and Pt/C catalysts, which was only 0.5%. And the prepared bimetallic Pd/Fe@N/C catalyst showed excellent catalytic reactivity with the conversion rate of nitrobenzene > 99%, and the selectivity of aniline 99% under mild reaction conditions of 0.8 MPa H₂ and 40 °C. A variety of halogenated and aliphatic nitro compounds were well tolerated and had been transformed to the corresponding target amine products with excellent selectivity. In addition, the novel N-doped graphene-encapsulated bimetallic magnetic Pd/Fe@N/C catalyst not only had magnetic physical properties, which was easy to separate, recover, and used for the recycling of the catalyst without metal leaching but also catalyzed highly selective

reductive amination of aromatics was a green, economical and environmentally friendly reaction with the only H₂O as a by-product.

KEYWORD

Nitrobenzene; Aniline; Hydrogenation; Heterogeneous catalyst; Transition metals; Graphene shelled catalyst

INTRODUCTION

Aniline, which serves as an important group of platform molecules, has been widely used in the synthesis of other high-value chemicals or products, such as polyurethane, dyes, rubber additives, explosives, medicines, pesticides, and fragrances^{1,2}. Some amine drugs³ for the prevention and treatment of diseases such as cardiovascular, cerebrovascular diseases, and cancer have always been occupied a high demand position in the market, especially with the raging new coronavirus, how to produce high-value aniline drug intermediates more efficiently and environmentally in the industry has become a research hotspot⁴. Traditionally, nitrobenzene hydrogenation methods mainly include metals (Fe, Zn, Sn)/acid reduction method, sulfide reduction method, and catalytic hydrogenation method. However, the production process of the first two methods usually produces harmful substances, including metal salt slag and sulfur-containing wastewater⁵⁻⁷, and such processes are affected by equipment corrosion and environmental pollution which are gradually replaced by more gentle procedures. Catalytic hydrogenation is an environmentally friendly method for preparing halogenated anilines. So far, the catalysts used for the hydrogenation of nitrobenzene are mainly noble Pt, Pd, Ru based catalysts, and some other non-noble Ni, Co and Fe based catalysts⁸⁻¹⁴. In the case of hydrogen as the hydrogen donor, some precious metals are often used for direct hydrogenation of nitroaromatics under high temperature and high pressure^{15,16}. According to the catalyst formulation, some metal-based catalysts, especially Pd¹⁷⁻¹⁹, showed good catalytic performance, but the current trend in the pharmaceutical and food industries is the progress of economical, green, and environmentally friendly processes. It is very important and desirable to develop more cost-effective and practical application methods. In order to improve the activity and recyclability of the catalyst, researchers immobilize nano-scale catalytically active metal

Pd on various supports²⁰⁻²². These heterogeneous catalysts showed good robustness and separability and had been used in industrial production, including fine chemical production.

As we all know, supported metal catalysts have attracted much attention because of their unique structure and better performance in certain catalytic reactions. Studies have shown that highly graphitized carbon promotes the reduction of nitrobenzene by enhancing electron transfer²³. Carbon materials have the advantages of flexibility for tailoring the pore structures and the potential for modification of the catalytic surface sites via introducing heteroatoms^{24, 25}. Up to now, there have been several developed methods to modify the properties of carbon materials via activation with varied reagents or doping with nitrogen, sulfur, phosphorus, etc²⁶⁻³⁰. According to the report, N modification is expected to increase the activity and selectivity of the catalyst by introducing more anchor sites, adjusting the electronic structure of the central metal, and interacting with the active center of protons³¹. The existence of N species in carbon materials changes the electronic state of carbon atoms and causes the graphite structure in carbon materials to expand and produce defect sites. These defect structures are essential for giving carbon materials superior catalytic activity and stability to selectively reduce nitrobenzene to aniline³².

Herein, we prepared a Pd/Fe bimetallic catalyst supported on N-doped carbon materials to reduce nitrobenzene to aniline under mild reaction conditions. The Pd content is only 0.5%. Through the catalytic effect of Pd and Fe bimetals, the N-doped C support can provide more active sites, and the catalyst is easy to separate and recover. The Pd/Fe@N/C catalyst showed the best catalytic activity under mild reaction conditions of 0.8 MPa H₂ and 40 °C, achieving >99% nitrobenzene conversion and 99% aniline selectivity. Many halogen-substituted and aliphatic nitro compounds have been studied, and target products with excellent selectivity have been obtained. As the catalyst has magnetic properties and is easy to separate, the flow reactor process is considered for further exploration in the later stage. The excellent mass and heat transfer performance of the continuous flow process will further make the reaction conditions milder, and strive

to achieve the conversion at room temperature.

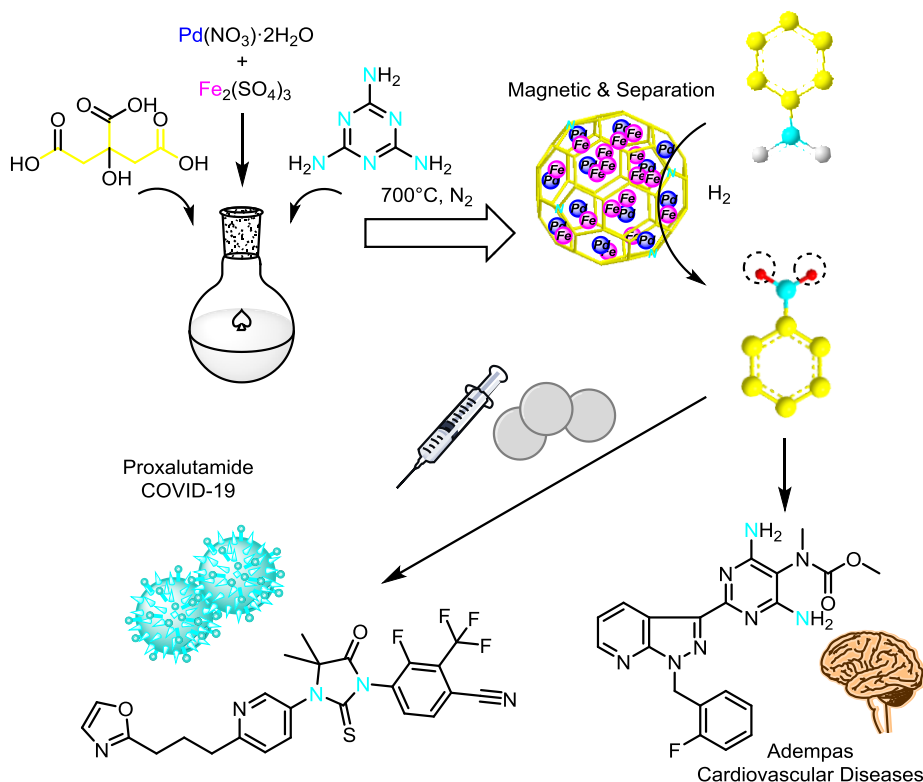


Figure 1. Preparation of Pd/Fe@N/C catalyst and its application in the synthesis of drug intermediate

2. EXPERIMENTAL SECTION

2.1 Materials

We bought the 1,3,5-trimethoxybenzene from Sigma Aldrich Co., Ltd., and $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (AR, Pd 18.09 wt. % in nitric acid), anhydrous citric acid (AR, $\geq 99.5\%$), Melamine (AR, 99%), commercial single ruthenium atom nitrogen-doped carbon catalyst were obtained from Shanghai Macklin Biochemical Co., Ltd.; H_2SO_4 (GR, 98%) was purchased from Sinopharm Chemical Reagent Co., Ltd.; aniline (AR, $\geq 99.0\%$), methanol (AR, 99.7%), commercial single palladium atom nitrogen-doped carbon catalyst, Raney nickel catalyst (20~40 meshes) were purchased from Aladdin (Shanghai) Chemical Technology Co., Ltd.; nitrobenzene (AR, 98.0%) was purchased from Tokyo Chemical Industry Co., Ltd.; Deionized water ($\sigma < 5 \mu\text{S/m}$) was self-made in the laboratory.

2.2 Preparation of Pd@C catalysts

In a typical synthesis procedure, palladium (II) nitrate hexahydrate ($\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$), $\text{Fe}_2(\text{SO}_4)_3$, melamine, and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) were dissolved in anhydrous ethanol (50 mL) at different ratios. The mixture was then aged at 70 °C for 4 h under stirring (300 rpm) until to obtain a green bubble gel, followed by drying at 100 °C for 24 h in a drying oven to remove the excess solvent. The obtained green solid was then calcined at a fixed bed at 700 °C for 3 h under a high-purity N_2 (99.999 %) flow of 40 $\text{mL} \cdot \text{min}^{-1}$. The heating rate was controlled at 2 °C $\cdot \text{min}^{-1}$. The obtained black solids were treated in 1 M H_2SO_4 aqueous solution at 70 °C until the solution was colorless to remove the insecure and uncovered Pd particles. The black solids were then fully washed with deionized water until the pH of the waste solution was 7. Finally, the black solids were dried at -48 °C for 12 h in a vacuum by using a freeze dryer. The dried black solids were denoted as Pd/Fe@N/C.

2.3 Hydrogenation of nitroarene in a batch reactor

The reaction was carried out in a stainless-steel autoclave (Shanghai Yanzheng Instrument Co., Ltd.) with a 10 mL well, a thermocouple, and a circulating water-cooling device. A glass lining was placed in the well, which contained a 10 mm magnetic stir bar, 0.5 mmol nitrobenzene, 10 mg catalyst, and 6 mL solvent. Then, the autoclave was sealed and purged with H_2 3 times under a pressure of 0.8 MPa, and pressurized with the set target H_2 pressure. Put the autoclave into the heating mantle and set the stirring speed to 300 rpm. The autoclave was preheated from room temperature to the target reaction temperature (the internal temperature detected by the thermocouple) at a rate of 2 °C $\cdot \text{min}^{-1}$. The reaction was carried out at the reaction temperature for the required time. After the reaction, the autoclave was cooled to room temperature and the remaining gas was discharged. The reaction solution was collected with a dropper and filtered. The catalyst was fixed on a magnetic stir bar and washed thoroughly with methanol and water. Then used a freeze dryer to dry the catalyst (together with a magnetic stir bar) under vacuum at -48 °C for 12 hours. The reaction product was identified by GCMS, and the yield of the reaction product was determined and calculated by GCMS using 1,3,5-trimethoxybenzene as the internal standard.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterizations of Pd/Fe@N/C catalysts

Figure 2 showed some representative scanning electron microscopy (SEM) images and high-angle annular dark-field-STEM (HAADF-STEM) images of nitrogen-doped graphene encapsulated Pd/Fe@N/C catalyst. As shown in **Figures 2a** and **2b**, the surface of the Pd/Fe@N/C catalyst had an obvious pore structure with the Pd and Fe particles dispersed evenly. The smaller Pd particles were evenly interspersed between the Fe particles, and the two particles were covered by a thin C shell to prevent the loss of the catalyst metal particles in the subsequent reaction. According to the HR-TEM analysis, the prepared N-doping Pd/Fe@N/C catalysts consisted of metal nanoparticles that were encapsulated by less than 5 graphene layers (**Figure 2c**), and >90% of metal species were encapsulated by a few graphene layers.

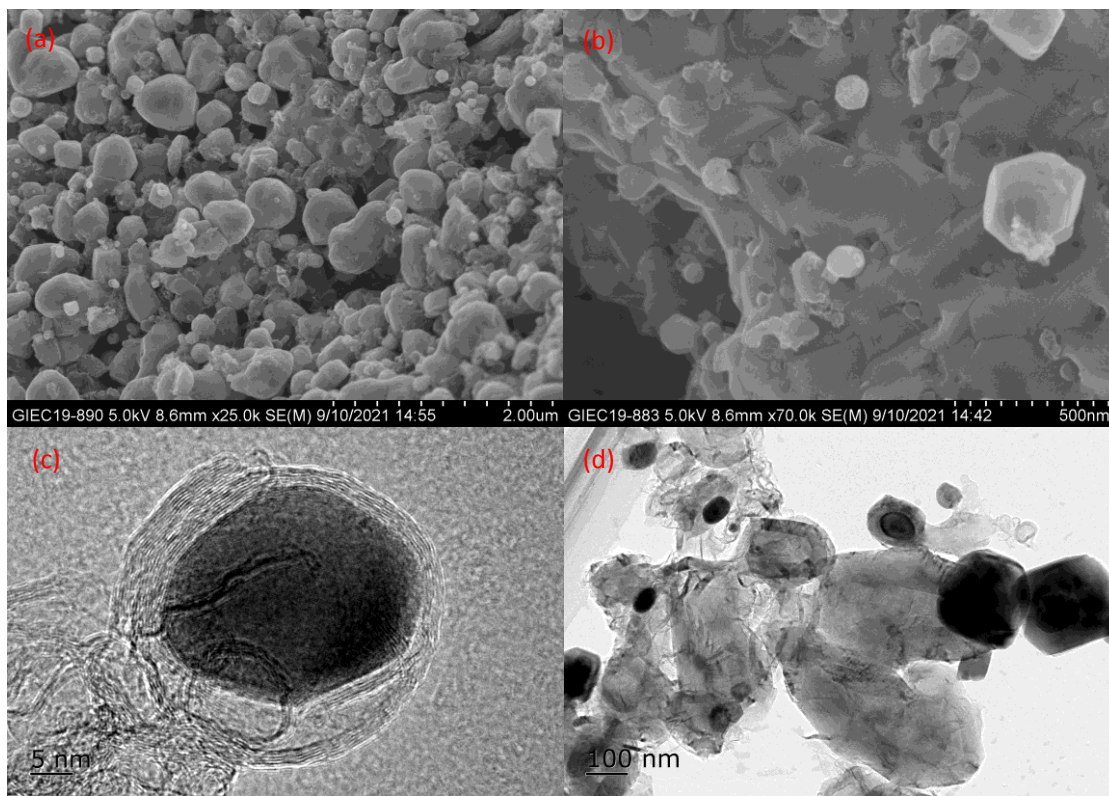


Figure 2. Catalyst characterization. Representative SEM images and HRTEM images of Pd/Fe@N/C catalyst.

The XRD spectrum showed that the graphitic carbon shell C (002) had a peak between 20 and 30, which confirmed that a thin graphene shell had been formed. Moreover, we could also observe the intensity peaks of Pd (011), Pd (011), N (002), and Fe₃O₄ species, which indicates the formation of N-doped Pd/Fe@N/C catalyst (**Figure 3**).

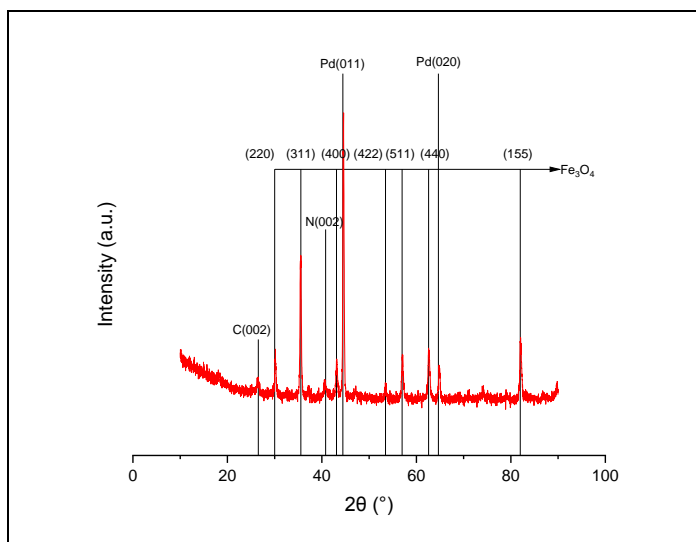
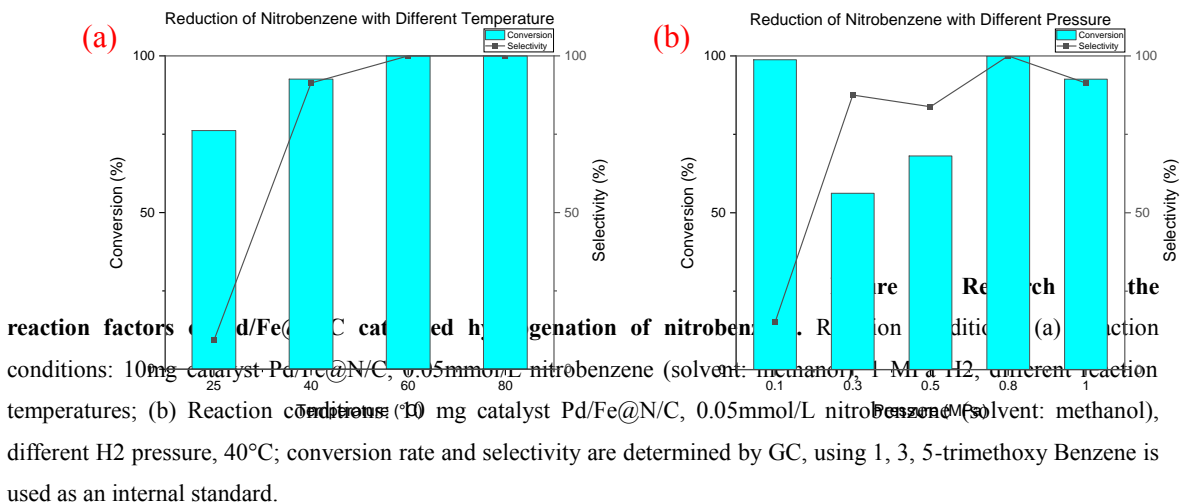


Figure 3. XRD images of Pd/Fe@N/C catalyst

3.2 Pd/Fe@N/C catalyzed selective hydrogenation of nitroarenes



After the successful synthesis of the N-doped graphene encapsulated Pd and Fe bimetallic catalyst Pd/Fe@N/C, we then tested its catalytic reactivity for the reductive amination of nitrobenzene. **Figure 4** showed the conversion rate and selectivity distribution of aniline at 1 MPa H₂ pressure and different temperatures. As shown in **Figure 4 (a)**, nitrobenzene produced many by-products during the reduction process at

room temperature (25°C), but only by raising the temperature to 40°C the selectivity can be increased to 91.34%, and the catalytic activity is also very large. The increase in degree is accompanied by a conversion rate of 92.60%. Similarly, during pressure screening, we found that many by-products are still generated at a hydrogen pressure of 0.1 bar. As shown in **Figure 4 (b)**, the overall conversion and selectivity are optimal at a hydrogen pressure of 0.8 bar. It is worth noting that the conversion rate of nitrobenzene at a pressure of 0.8 Mpa is higher than that at a pressure of 1 MPa. This is because competitive adsorption partly weakens the bond between each adsorbate and the surface. Specifically, it is due to the competitive adsorption of phenyl and N-containing groups in the process of PhNO₂ hydrogenation. The weak bond between the adsorbate and the surface is more conducive to association reactions such as hydrogenation. Since hydrogenation usually requires energy to partially destroy the bond between intermediate and surface atoms to form the bond between intermediate and hydrogen, the weaker the bond between intermediate and surface atoms, the lower the hydrogenation barrier. Therefore, the hydrogenation barrier becomes lower under actual reaction conditions. Interestingly, the solvent has a great influence on the reduction of nitrobenzene. In the solvent range of **Table1 Entry 4~10**, only when the solvent is alcohols (**Entry 4, 5, and 10**) can the catalyst have a reduction effect on nitrobenzene. To explore whether hydrogen and methanol are used as a common source of hydrogen, we conducted a set of control experiments (**Entry 11**). The reductive amination of nitrobenzene was carried out with methanol as a solvent under a nitrogen pressure of 0.8 bar. It was found that no product aniline was formed, which shows that H₂ is true as the only hydrogen source. The solvent can not only promote the dispersion of the reactants and enhance the mass transfer process in the catalytic reaction but also change the path of the reaction kinetics³³. The significant difference in reactivity is only due to the difference in solvation of adsorbed hydrogen. In addition, the polarity of solvent can effectively adjust the bonding between reactant/ intermediate and Pd³⁴. The hydrogenation kinetics of nitro compounds on palladium catalyst supported on coal was studied³⁵⁻³⁷. Klyuev³⁵ found that the hydrogenation of nitrobenzene is a first-order reaction for catalyst and hydrogen, and a pseudo-zero-order reaction for nitrobenzene. So the significant influence of the solvent is assumed to be due to the sol pores changing the adsorption configuration of reducing

groups on the transition metal surface ³⁸, Changed the potential energy field formed by the hydrogen bond between the original solvent and the organic matrix ³⁹⁻⁴¹. It can be concluded that the hydrogen bond with the metal is weaker to a certain extent, which is beneficial to the hydrogenation rate, and it is consistent with the phenomenon in the pressure screening process. In addition to the screening of reaction conditions, we also prepared some catalysts for control reactions. The results showed that although the amount of active metal Pd was reduced to 10% equivalent of Pd@N/C catalyst, the catalytic hydrogenation activity of p-nitrobenzene was greatly improved due to the bimetallic catalytic effect of transition metal Fe. However, when pure Fe was used as the active center, no matter what the valence state of the Fe central atom is, the catalytic hydrogenation of p-nitrobenzene cannot be exerted. Therefore, both Pd and Fe metals play an indispensable role and greatly improve the catalytic activity while reducing the content of the noble metal Pd to a great extent.

Table 1. Pd/Fe@N/C catalyzed nitrobenzene hydrogenation catalyst, solvent, and pressure type influence research.

Entry	Cat.	Solv.	Temp. (°C)	Pre. (MPa)	Time (h)	Conv. (%)	Sel. (%)
1	Pd@N/C ^a	MeOH	60	1	4	45.54	>99
2	Fe(ferrous)@C ^b	MeOH	60	1	4	-	-
3	Fe@C ^c	MeOH	60	1	4	-	-
4	Pd/Fe@N/C	MeOH	60	1	4	>99	>99
5	Pd/Fe@N/C	EtOH	40	0.8	4	12.72	78.95
6	Pd/Fe@N/C	DCM	40	0.8	4	-	-
7	Pd/Fe@N/C	TOL	40	0.8	4	-	-
8	Pd/Fe@N/C	EtOAc	40	0.8	4	-	-
9	Pd/Fe@N/C	CYH	40	0.8	4	-	-
10	Pd/Fe@N/C	IPA	40	0.8	4	6.03	90.65
11	Pd/Fe@N/C	MeOH	40	0.8 ^d	4	-	-

a. The amount of Pd added is 10 mol equivalent of Pd/Fe@N/C catalyst; b. The source of Fe is FeSO₄·7H₂O, and the amount of Fe added is the same as that of the Pd/Fe@N/C catalyst; c. The source of Fe is Fe₂(SO₄)₃, and the amount of Fe added is the same as that of the Pd/Fe@N/C catalyst; d. The source of pressure is N₂ instead of H₂

We have also studied many halogen-substituted and aliphatic nitro compounds and obtained target products with excellent selectivity (**Figure 5**). Both industrially relevant and structurally challenging nitrobenzene derivatives have achieved effective amination, and the corresponding aniline has been produced in good to excellent yields. Fluoride and chloride substrates are well tolerated, aliphatic nitro compounds can also withstand the reaction conditions, and the corresponding anilines can be obtained with excellent yields. Even cycloalkyl nitro compounds with various ring sizes can be successfully transferred to aniline.

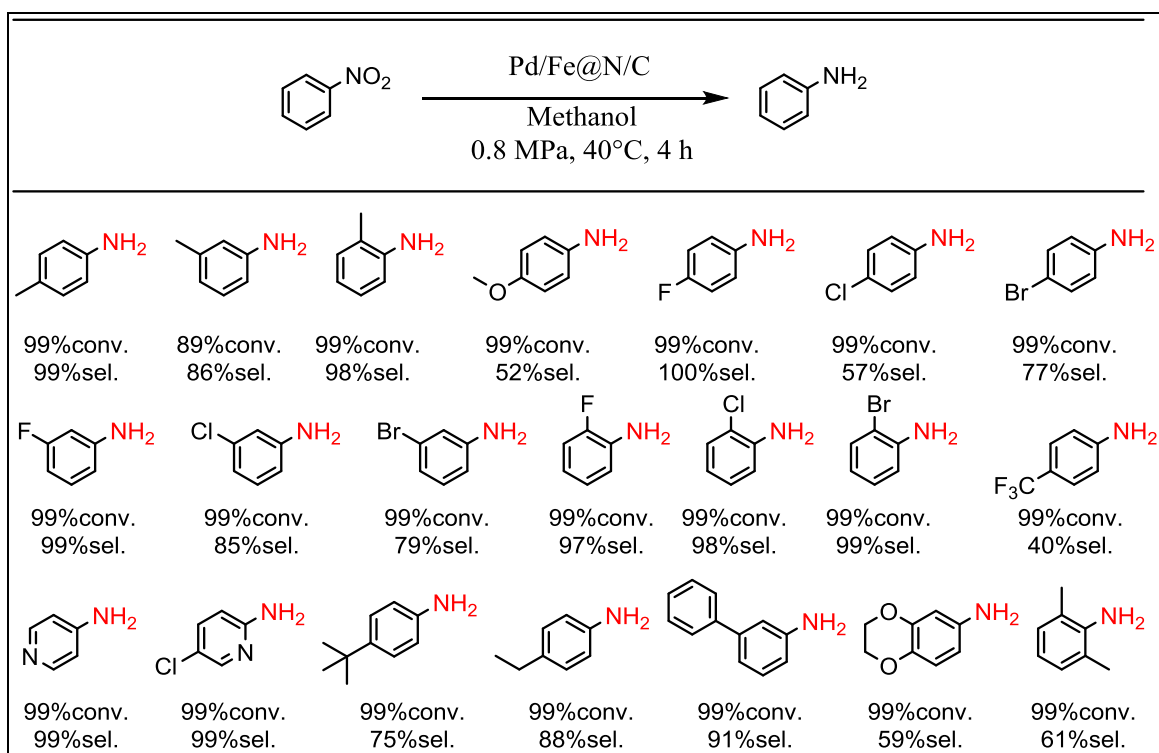


Figure 5. Reaction conditions: 10mg catalyst Pd/Fe@N/C, 0.05mmol/L nitrobenzene (solvent: methanol), 0.8 MPa H₂, 40°C; conversion rate and selectivity are determined by GC, using 1, 3, 5-trimethoxy benzene is used as an internal standard.

3.2 Proposed mechanism of Pd/Fe@Ni/C catalyzed hydrogenation of nitrobenzene

Based on the above experiments and analysis, a proposed mechanism was proposed as illustrated in **Figure 6**. Unlike the previously reported Haber reaction mechanism⁴², the reduction of nitrobenzene could be achieved through the phenylhydroxylamine (PhNHOH) intermediate but not via the PhNO intermediate⁴³⁻⁴⁵. First, the substrate was absorbed on the catalyst active species and the N-O bond was activated and broke with the help of Pd-H species. Then the formed PhNOOH* intermediate could directly

undergo hydroxyl elimination reaction to produce the PhNO^* intermediate, or it could be further reduced to form PhN(OH)_2^* intermediate, which was further subjected to dehydroxylated reaction to form the PhNOH^* intermediate. It has been known that the highest energy barrier required for the hydrogenation of PhNHOH^* intermediate to PhNH^* intermediate is the rate determining step for the final reduction of hydroxylamine intermediate to aniline. However, based on the above experimental studies, we found that if the hydrogen pressure was too high, the activated H^* might occupy the reactive sites of the catalyst, thereby hindering the dissociation reaction of the N-O bond to a certain extent, and forming intermediates that were more difficult to dissociate.

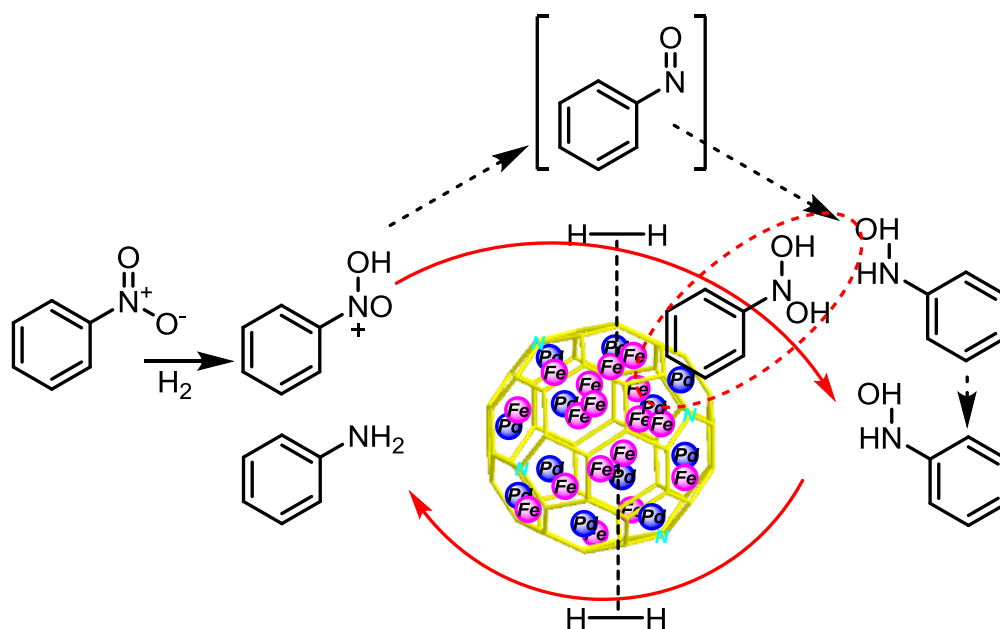


Figure 6. Proposed mechanism of Pd/Fe@N/C catalytic hydrogenation of nitrobenzene to aniline. The dashed path indicates the Hubble direct path, and the red path indicates the broken key path

4. CONCLUSION.

We prepared a Pd/Fe magnetic bimetallic catalyst supported on N-doped carbon materials to reduce nitrobenzene to aniline under mild conditions without the formation of by-products. The Pd content is only 0.5%. Through the catalytic effect of Pd and Fe bimetals, the N-doped graphene support can provide more active sites, and the magnetic catalyst is easy to separate and easy to recover. For the hydrogenation of nitro compounds, Pd/Fe@N/C shows the best catalytic activity under mild reaction conditions of 0.8 MPa H_2 and 40°C , achieving 100 mol% nitrobenzene conversion and 99% aniline

selection. Many halogen-substituted and aliphatic nitro compounds have been studied, and target products with excellent selectivity have been obtained. Because the catalyst is magnetic and easy to separate, the continuous flow process is considered for further exploration in the later stage. The excellent mass and heat transfer performance of the continuous flow process will further make the reaction conditions milder, and strive to achieve the conversion at room temperature.

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AUTHOR CONTRIBUTIONS J. G. L. and L. L. M supervised and designed the research. S.S.L. performed the experiments and data analysis. S.S.L. and J. G. L. co-wrote the original manuscript. J.G.L. reviewed and corrected the manuscript. All authors discussed the results and assisted during manuscript preparation.

COMPETING INTERESTS The authors declare no competing financial interests.

DATA AVAILABILITY Data supporting the findings of this study are available from the corresponding authors upon reasonable request.

ADDITIONAL INFORMATION Correspondence and requests for materials should be addressed to J. G. L. or L. L. M.

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