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ARTICLE

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Rational design of heterogeneous non-noble metal catalysts as highly efficient and selective catalysts for hydrogenation of nitroarenes with hydrogen as reducing agent is currently a great challenge, which has attracted a great deal of attention. Herein, a new strategy for achieving atomic dispersion of Ni atoms on nitrogen-doped porous carbon (Ni-N-C) with a specific surface area of up to 810 m²g⁻¹ and nickel loading as high as 4.4 wt% are developed, yielding the high activity, chemoselectivity, and reusability catalysts in hydrogenation of nitroarenes using hydrogen as reductant with turnover of number (TON) value (84) and turnover of frequency (TOF) value (8.4 h⁻¹) for the first time. The Ni single atoms anchored on N-doped porous carbon by binding with nitrogen/carbon have been proven to be the active sites. Importantly, the Ni-N₃ active specie is found to contribute more activity compared with Ni-N2 and Ni-N4. Density functional theory (DFT) calculation also reveals that the Ni-N₃ structure exhibits the highest activity according to the lowest adsorption energy and the longest elongation N-O bonds of nitrobenzene, originated from the induced charge transfer. This work opens a new route for rational design and accurate modulation of nanostructured organic molecular transformation catalysts at the atomic scale.

1. Introduction

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Synthesis of aniline derivatives have attracted much attention owing to its the important intermediates for the manufacture of pharmaceuticals, agrochemicals, pigments dyes and fine chemicals.¹ The traditional method is reduction of the corresponding nitroarenes with stoichiometric reducing agents, such as sulfides, Fe, and Zn.² Such production processes show low conversion rate and produce large amounts of waste acids and residues. Although noble metal catalysts, such as Pd, Au, and Ru, have been used in hydrogenation of nitroarenes to synthesize functionalized anilines due to their extraordinary activities,³ their high cost greatly limits their widespread application, and it is a great challenge for chemoselectivity reduction of nitroarenes bearing reducible groups (C-Br, C=O, C=C, and so on).⁴ Therefore, it is necessary to develop the high active and chemoselective non-noble metal catalysts.

In recent years, many non-noble metal catalysis systems for

nitroarenes reduction reaction, such as Fe₂O₃, Ni-NiFeO₄, Co- Co_3O_4 , carbon materials, and so on_5^5 have been developed.

Herein, we propose a strategy to facilitate construction of an effective catalysis system based on atomically dispersed Ni on



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Among the above catalysts, great efforts have been devoted to studying the heteroatom-doped carbon materials due to their cheap, stable, biocompatible, environment-friendly and readily available properties.^{5d} Although N-doped graphene, carbon nanotubes (CNTs) and N-doped CNTs have been used in reduction of nitroarenes, the strong reduction agents, such as NaBH₄ and hydrazine hydrate, are inevitably used.^{5e,6} It remains a challenge for selective hydrogenation of nitroarenes in using the cost-effective H₂ by designing heteroatom doped carbon materials. Based on these considerations, employing Ndoped carbon as dispersion for abundant no-noble metal catalytic active site is the promising candidate to enhance the catalytic activity. The M-N-C (M refers to transition metal) single-atom catalysts (SACs) have emerged as a new frontier in the field of heterogeneous catalysis due to their remarkable catalytic performances and maximized atom utilization.⁷ The M-N-C SACs have exhibited superior activities in CO2 reduction, oxygen reduction reaction (ORR), hydrogen evolution reaction (HER) and other important reactions.8 To date, the M-N-C SACs used in hydrogenation of aromatic nitro compounds have never been reported yet. Moreover, the structure of activity site in M-N-C SACs for such reaction is ambiguous, thereby hindering the further application of these catalysts in organic molecular transformation reactions.

ARTICLE

N-doped porous carbon (Ni-N-C) for hydrogenation of nitroarenes to arylamine using H₂ as reduction agent. As a result, a catalyst with the Ni loading of up to 4.4 wt%, a huge specific surface area (810 m²g⁻¹) and lamellar hexagonal porous structure is derived from the pyrolysis of a mixture of a coordinatively saturated NiCl₂ with 1,10-phenanthroline organometallic compound and inexpensive porous MgO powder at 700 °C. It is denoted as Ni-N-C-700. Extended X-ray absorption fine structure (EXAFS) spectra illustrate that such a facile method is powerful to tune the coordination numbers of Ni with N of the Ni-N-C catalysts through controlling the calcination temperature without immensely influencing the morphology. The Ni-N-C-700 catalyst also shows good functionalized group tolerance in contrast to noble metal catalysts, high chemoselectivity in the presence of reducible groups, excellent stability with no significant decrease in activity after 5th consecutive runs, which exhibits superior performance than those of previously reported no-noble metal catalysts under mild conditions with molecular hydrogen as reductant. The control experiments have been prove that Ni single atoms anchored on N-doped porous carbon by binding with nitrogen/carbon is the active sites. Density function theory (DFT) caculation reveals the sequence of Ni-N1, Ni-N2, Ni-N3, and Ni-N₄ activities in current hydrogenation reaction. Our strategy may open up an effective routine for general controllable construction of atomic-scale M-N-C active sites for organic molecular transformation reaction.

2. Materials and methods

2.1 Materials

All the chemicals are analytical grade and without further purification. Aromatic nitro compounds, 1,10-phenanthroline, triphenylmethane (TPM), (J&K Scientific), MgO powder (Sinopharm Chemical Reagent Beijing Co., Ltd), silica gel (Alfa Aesar, Johnson Matthey Company), HCl, NiCl₂·6H₂O, H₂SO₄, (Beijing Chemical Works).

2.2 Preparation of MgO template

Porous MgO layers were prepared according to the previously reported literature.⁹ The MgO powder (30 g) was mixed with deionized water (300 mL) accompanied with ultrasonic agitation. The mixture was boiled for 48 hours in a reflux apparatus, and then the white solid was filtered and dried at 80 °C overnight. The obtained bulk was then smashed into fine powder and heated at 500 °C for 2 h.

2.3 Synthesis of atomically nickel-dispersed Catalysts

The procedure for the preparation of the catalysts was described as follows: 1 mmol NiCl₂· $6H_2O$ and 3 mmol 1,10-phenanthroline were dissolved in 100 ml ethanol for 60 min under constant stirring. Then MgO template (1 g) was added and the mixture was stirred overnight. After ethanol was removed by rotary evaporators, the green solid was ground into fine powder and pyrolyzed at 600 °C, 700 °C and 800 °C for 2 h under argon. The samples prepared were appointed as Ni-N-C-600, Ni-N-C-700 and Ni-N-C-800 respectively. After cooled to room temperature, obtained black powder (labeled as Ni-N-C-

MgO) was washed by 1 mol/L hydrochloric acid for $1_{\rm rh}$ and $1_{\rm rh}$ mol/L H₂SO₄ at 80 °C for 2 h, followed by the roughly washing with deionized water and ethanol. For comparison, Nitrogendoped porous carbon (labeled as N-C) with the same procedure was prepared except for the absence of NiCl₂·6H₂O.

2.4 Synthesis of Ni-NC Catalysts

Porous carbon was prepared according to the literature previously reported by our research group.¹⁰ Firstly, 5 g MgO template and 3 g TPM were first mixed together in ethanol under magnetic stirring at room temperature. The obtained MgO/TPM composite was pyrolyzed at 700 °C for 2 h under argon. After cooling to room temperature, the porous carbon was obtained by removed the MgO template with the hydrochloric acid. Then, oxidation treatment of porous carbon material with mixed acid of sulfuric acid and nitric acid. To prepare metallic Ni-nanoparticle-decoratednitrogen-doped carbon (Ni-NC), 200 mg of oxidized porous carbon material was first dispersed in ethanol by ultrasonication, followed by addition of 100 mg of NiCl₂·6H₂O. After ethanol was removed by rotary evaporators, the dried product was ground with 500 mg of melamine into a homogeneous mixture, followed by a pyrolyzed process at 700 °C for 2 h under argon atmosphere. The Ni-NC was obtained by cooling to room temperature.

2.5 Catalytic hydrogenation of nitrobenzene

The catalytic hydrogenations were carried out in a 30 mL stainless steel reactor equipped with a magnetic stirred. Typically, 0.25 mmol nitroarenes, 5 mL ethanol and an appropriate amount of catalyst were charged into the reactor. The reactor was flushed three times with H_2 and N_2 before the required H_2 pressure was introduced. The reactors were then placed into an oil bath, heated to desired temperature and the reactions were stirred for 10 h. After completion of the reaction, the mixture was cooled to room temperature. Filtered the catalyst, the organic phase was concentrated, and the residue was purified by column chromatography (petroleum ether/ethyl acetate mixture) to give the isolated yield.

2.6 Characterization

The morphology and structure of the samples were characterized using a Hitachi SU8010 scanning electron microscope (SEM) operated at 3.0 kV and JEM-2100 transmission electron microscope (TEM) operated at 120.0 kV. The TEM images and SAED patterns were taken on JEM-2100 operated at 120.0 kV. The HAADF-STEM images and EDS maps were taken on an FEI microscope of Titan Cubed Themis G2 300 operated at 200.0 kV. X-ray photoelectron spectroscopy (XPS) measurements was carried out on Thermo Fisher K-Alpha American with an Al Ka X-ray source. Powder X-ray diffraction patterns of samples were recorded on Bruker D8 Advance Germany with Cu Ka radiation. BET specific surface area, pore radius and volume are analyzed with N₂ adsorption/desorption isotherms at 77 K on a SSA4200 instrument (Beijing Builder Electronic Technology Co., Ltd.). The Ni concentration of the sample was conducted on the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES Optima 7300V). Raman spectra were recorded on HORIBA Xplora PLUS Raman microscope system with Ar Published on 14 January 2019. Downloaded on 1/21/2019 12:38:16 AM

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laser excitation at 532 nm laser. The X-ray absorption fine structure spectra were performed at the beamline 1W1B station of the Beijing Synchrotron Radiation Facility (BSRF), China. The energy of the storage ring electron beam was 2.5 GeV with a ring current of ~250 mA. The hard X-ray was monochromatized with Si(111) double-crystal monochromator and the detuning was done by 30% to remove harmonics. The data collection was carried out in transmission mode using ionization chamber for Ni foil, NiPc, and in fluorescence excitation mode using a Lytle detector for Ni-N-C materials. All spectra were collected in ambient conditions. The acquired EXAFS data were processed and fitted according to the standard procedures using the Athena and Artemis implemented in the IFEFFIT software packages.

2.7 Computational details

All the electronic structure and energy calculations were performed by the spin-polarized density functional theory (DFT) by using Vienna ab initio simulation package (VASP).¹¹ PAW potentials were used to describe ion cores and valence electrons interactions.¹² The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof¹³ was selected to describe the exchange-correlation functional. A kinetic energy cut off of 400 eV was used with a plane-wave basis set. The integration of the Brillouin zone was conducted using a 1×1×1 Monkhorst-Pack grid.¹⁴ The convergences of the force and the total energy were set as 0.05 eV/Å and 1.0×10⁻⁵ eV/atom, respectively.

The typical Ni-N_x (x=1-4) substrates were established according to the previous studies based on 5×5 graphene. All atoms were allowed to relax. vdW interaction was employed in our calculations by a semiempirical DFT-D2 force-field approach.

To study the stability of nitrobenzene and H_2 on Ni-N_x surface, the adsorption energy was defined as,

 $E_{ads} = E_{substrate+n} - E_n - E_{substrate}$ (1) $E_{ads(co-adsorption)} = E_{substrate+H2+n} - E_{H2} - E_n - E_{substrate}$ (2)

where $E_{substrate+n}$, $E_{substrate+H2+n}$, E_n , E_{H2} and $E_{substrate}$ correspond to the total energies of substrate and nitrobenzene molecule, substrate and nitrobenzene and H₂ molecule, a gas phase nitrobenzene, a gas phase H₂ molecule and an isolated substrate, respectively. A negative value indicates an exothermic chemisorption.

3. Results and discussion

3.1 Characterizations of Ni-N-C catalysts

The single Ni atom catalyst was achieved by pyrolysis of coordinatively saturated NiCl₂ with 1,10-phenanthroline dispersed on the surface of hexangular lamella porous MgO at 700 °C under Ar atmosphere and acid leaching (Fig. 1a). The SEM and TEM images of Ni-N-C-700 catalyst (Fig. 1b and c) show laminated hexagonal appearance, which is derived from the MgO template (Fig. S1a and b). Fig. 1d shows that abundant mesopores are located on the layers of the carbon sheets. Notably, no metal particles can be observed, and the sample has a poor crystallinity as proven by the selected-area electron diffraction (SAED) pattern. These findings suggest that

atomically dispersed Ni sites may exist in vitheric carbon framework, which are further confirmed^{0.1}by^{9/}aberrations corrected high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images (Fig. 1e and f). The monodispersed isolated bright dots in the carbon matrix are corresponding to single Ni atoms, because Ni is heavier than N and C. Meanwhile, energy-dispersive X-ray spectroscopy (EDS) mapping with STEM shows that Ni and N are uniformly distributed in the entire architecture (Fig. 1g). Therefore, it is confirmed that atomically dispersed Ni sites on N-doped porous carbon (NC) are successfully obtained. For comparison, Ni-N-C-600 and Ni-N-C-800 samples were synthesized by the same procedure with 600 °C and 800 °C, and the NC-supported Ni nanoparticles (Ni-NC) were also prepared. These control samples have the same morphologies as Ni-N-C-700 (Fig. S2, S3 and S4). Ni-N-C-600 contains only atomically dispersed Ni sites and no nanoparticles exist in it (Fig. S2), which illustrates that the Ni nanoparticles (Ni NPs) can be efficiently removed by acid leaching. But Ni-N-C-800 contains not only atomically dispersed Ni sites but also Ni NPs (Fig. S3). The reason for Ni-N-C-800 contain Ni NPs whereas Ni-N-C-600 and Ni-N-C-700 inexistence Ni NPs is due to that high crystallinity carbon layer on the surface of some Ni NPs is formed at 800 °C, which can prevent the acid leaching from washing away the Ni NPs.15 Fig. S4 shows the Ni nanoparticles are dispersed on the surface of Ni-NC.



Fig. 1 (a) Schematic illustration for synthesis of Ni-N-C catalysts. (b) SEM image, (c) TEM image (inset shows the corresponding SAED pattern), and (d) high-magnification TEM image of Ni-N-C-700. (e), (f) Aberration corrected HAADF-STEM images of Ni-N-C-700, in which single Ni atoms are clearly seen. Some of them are highlighted by red circles. (g) HAADF image and its corresponding EDS maps revealing that the Ni and the N elements are homogeneously distributed in Ni-N-C-700.

The as-synthesized catalysts are also studied by X-ray diffraction (XRD), Raman spectroscopy, and Brunauer-Emmett-Teller (BET) measurement. As shown in Fig. 2a, only the (002) and (004) planes of carbon are observed at 26.2° and 44.0° in Ni-N-C-600 and Ni-N-C-700 samples.^{7e,8d} In contrast, the metallic Ni diffraction peaks are distinctly observed in Ni-

ARTICLE

N-C-800 and Ni-NC. These results are consistent with the TEM and SAED results. The BET adsorption-desorption isotherms also demonstrate that the Ni-N-C-600, Ni-N-C-700, and Ni-N-C-800 catalysts possess a mesoporous structure with specific surface area (SSA) of 750, 810 and 790 m²g⁻¹, respectively (Fig. S5). Notably, the 3D porous structure of catalysts with high SSA not only is beneficial to the adsorption reactant and mass transfer but also gives accessibility to the active sites for the hydrogenation reaction. Moreover, the Raman spectra (Fig. S6) show that two conspicuous peaks are attributed to the D band at about 1350 cm⁻¹ for the disordered carbon, edge defects, and other defects and the G band at about 1580 cm⁻¹ for E_{2g} vibrational mode in the sp²-bonded graphitic carbon, respectively.¹⁶

ARTICLE

To confirm the chemical state and coordination of the Ni atoms in Ni-N-C catalysts, the Ni K edge X-ray absorption near the edge structure (XANES), extended X-ray absorption fine structure (EXAFS), and X-ray photoelectron spectroscopy (XPS) have been performed, as shown in Fig. 2c-2f and Fig. S7-S8. The near edge of Ni-N-C-600, Ni-N-C-700 and Ni-N-C-800 are between those of Ni foil and NiPc, suggesting that Ni in the pyrolysis products is in the intermediate valence state.^{8c,8d,17} This is due to that the neighboring N atoms partially deplete Ni free electrons through the valence bond.8c It is evident that the Ni-N-C-800 near-edge absorption is closer to Ni foil, due to the presence of metallic nickel in Ni-N-C-800. As shown in Fig. 2d, Ni metal exhibits a typical first shell Ni-Ni pair at ~2.18 Å, while Ni-N interaction in NiPc locates at ~1.47 Å. The peak located at ~1.4 Å for all Ni-N-C samples corresponds to the Ni-N scattering path, indicating that the Ni atoms are atomically dispersed and bonded with N atoms in the catalysts.8c,18 Ni nanoparticles coexistence with single Ni atoms in Ni-N-C-800 has been further identified due to the presence of Ni-Ni scattering. The quantitative structure of Ni species investigation was carried out by the EXAFS fitting (Fig. S8). The coordination numbers of Ni in Ni-N-C-600, Ni-N-C-700, and Ni-N-C-800 are 3.7, 3.3, and 2.6, respectively (Table S1). These results demonstrated that Ni atoms are atomically dispersed in the N-doped porous carbon, which are mixed with two-fold, three-fold and four-fold coordinated by N atoms. Moreover, the coordination numbers of Ni-N is reduced along with the temperature increased.¹⁹ This result illustrates that some Ni-N bonds are broken with increasing the pyrolysis temperature. It also explains that the Ni-N bonds further breaks with the pyrolysis temperature up to 800 °C, which tend to the formation of the Ni NPs and the high crystallinity carbon layer on the surface of some Ni NPs. X-ray photoelectron spectroscopy (XPS) has been further used to demonstrate the above results. The binding energy of Ni 2p3/2 in pyrolysis products are around 855.0 eV, higher than that of metallic Ni⁰ (~853.0 eV) and lower than that of Ni^{2+} in NiPc (~855.7 eV), showing the valence states of Ni species in pyrolysis products between 0 and +2 (Fig. 2e), 8c, 8d, 17 being in agreement with the XANES results. The Ni contents in Ni-N-C-600, Ni-N-C-700, Ni-N-C-800, and Ni-NC measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) are 4.9, 4.4, 3.6, and 10.3 wt%, respectively, which are consistent with XPS

results, as summarized in Table S2. Fig. 2f and Fig. S7be show that the high-resolution XPS N1s spectrum the observation of the five nitrogen configurations, originating from pyridinic-N (398.5 \pm 0.2 eV), Ni-N (399.4 \pm 0.2 eV), pyrrolic-N (400.6 \pm 0.2 eV), graphitic-N (401.3 \pm 0.2 eV) and N-oxidized (> 403 eV), respectively.²⁰ The presence of Ni-N suggests that these nitrogen atoms bind to Ni atoms directly, and the binding energy of Ni-N is similar to that of in NiPc (Fig. S7c).²¹ Moreover, the contents of different nitrogen configurations are summarized in Table S3. The ratio of Ni-N specie to Ni is decreased with increasing the pyrolysis temperature from 600 to 800 °C, indicating that some Ni-N coordination bonds are broken, which neatly supports EXAFS fitting results.



Fig. 2 (a) XRD patterns of Ni-N-C-600, Ni-N-C-700, Ni-N-C-800 and Ni-NC. (b) Nitrogen adsorption isotherms of Ni-N-C-600, Ni-N-C-700, and Ni-N-C-800 measured at 77 K. (c) Ni K-edge XANES of the Ni-N-C catalysts and Ni foil and NiPc as the references, (d) Fourier transformed EXAFS spectra of Ni K-edge for Ni-N-C catalysts and corresponding reference samples. (e) Ni 2p high-resolution XPS surveys of Ni-N-C catalysts, Ni-NC and NiPc. (f) N1s XPS spectra of Ni-N-C.

3.2 Hydrogenation of nitroarenes

The catalytic activity of as-synthesized samples are initial evaluated using the hydrogenation of 4-chloronitrobenzene with 5 equiv. sodium borohydride as reducing agent (Table S4). The Ni-N-C-700 catalyst exhibits higher activity compared to that of Ni-N-C-600 and Ni-N-C-800, which is superior to other carbon catalysts (Table S5). We also extend the Ni-N-C-700 catalyst to various nitroarenes, and the corresponding aromatic aniline is formed smoothly in excellent yield (Table S6). Considering the high catalytic activity of Ni-N-C-700, the weaker reductants H₂ is used to examine the hydrogenation of 4-chloronitrobenzene (Table 1). It is interesting to find that the reaction can complete by using 5 mg Ni-N-C-700 catalyst to catalyze 0.25 mmol of 4-chloronitrobenzene with 3 MPa H₂ in ethanol at 120 °C for 8 h (entry 1). When decreasing the H₂

pressure, catalyst amount, and reaction temperature, the conversion of 4-chloronitrobenzene is incomplete (entries 2-4). However, this process can be accomplished with prolonging the reaction time (entry 5). Other solvents, such as H₂O, EtOAc, and THF, are inferior to EtOH in current reaction (entries 6-8). Generally, the hydrogenation activity of nitrobenzene exhibits a positive relation with the solvent polarity. However, both dispersibility of the catalyst and solubility of the reactant performances are very important for selecting solvent of heterogeneous catalysis reaction system. In such system, the low catalytic activity of hydrogenation of nitrobenzene reaction with water as solvent is probable due to the poor dispersibility performance of catalyst and the low solubility of nitrobenzene in water.²² In order to identify the active species derived from the Ni-N-C catalysts, a series of control experiments, such as using NiCl₂, NiCl₂ and 1,10-phen, N-C and Ni-NC as catalysts have been carried out. The reaction cannot proceed in the cases of using NiCl₂, NiCl₂ and 1,10-phen as catalysts (entries 10-11), and the N-C and Ni-NC catalysts show extremely low activities, affording 4-chloroaniline in 21% and 38%, respectively (entries 12-13). It is demonstrated that the N doping and the Ni nanoparticles are contribute little to such reaction. Moreover, the Ni-N-C-600 and Ni-N-C-800 catalysts show lower activity compared with Ni-N-C-700, giving 4-chloroaniline in 82% and 63%, respectively (entries 14-15). However, when addition of NaSCN to the reaction system, the yield of 4-Chloroaniline decreases dramatically to 28% (entry 16). These results indicate that Ni single atoms bonded to N atoms in the porous N-doped carbon framework are critical active sites for impelling this reaction. More importantly, the Ni-N₃ active species probably show better activation performance than Ni-N2 and Ni-N4 due to the fact that the higher content of Ni-N₃ exists in Ni-N-C-700 compared with that of Ni-N-C-600 and Ni-N-C-800. Additionally, in order to predict the possible path of reaction, the two intermediates, nitrosobenzene and azoxybenzene, have been observed by CC-MS after the reaction carried out in 3 h (Fig. S9). Therefore, we can conclude that the reaction mechanism probably works in hydroxylamine and diazene oxide two pathways (Fig. S10).

Various nitroarenes have been further extended in catalysis by Ni-N-C-700 catalyst under the optimized reaction condition. The catalyst shows good activity for the hydrogenation of both electro-donation and electro-withdrawing substituted nitroarenes (Table 2). It is noteworthy that the chloro, bromo substituted nitroarenes can be reduced without undergoing dehalogenation (entries 2-3). The hydrogenation of nitrile, keto, carboxyl and ester substituted nitroarenes can take place selectivity without reduction of these reducible functional groups in aromatic nitro substrates (entries 8-11). The hydrogenation of nitrostyrene reaction is further carried out to evaluate the selectivity of Ni-N-C-700. Only 4-nitrostyrene and 4-vinylaniline were detected by GC-MS in the filtrate after the reaction (Fig. S11), and 91% of 4-vinylaniline isolated yield is obtained (entry 12). These results illustrate that Ni-N-C-700 catalyst exhibits high activity for hydrogenation of nitroarenes and great chemoselectivity. We have also compared the Accepted Manuscript

efficiency of Ni-N-C-700 with that of knownvicatalystsolin literatures (Table S7). We found that Ni-NºC19003eafaalyst03664K

Table 1 Evaluation of reaction	n conditions for the reduction of 4-chloron	itrobenzeneª

$CI \longrightarrow NO_2 \xrightarrow{Catalyst, H_2} CI \longrightarrow NH_2$							
Entry	Catalyst	P (Mpa)	Usage (mg)	<i>T</i> (h)	<i>Т</i> (°С)	Yield⁵ (%)	
1	Ni-N-C-700	3	5	8	120	99	
2	Ni-N-C-700	2	5	8	120	78	
3	Ni-N-C-700	3	5	8	110	82	
4	Ni-N-C-700	3	4	8	120	81	
5	Ni-N-C-700	3	4	10	120	99	
6	Ni-N-C-700	3	4	10	120	85°	
7	Ni-N-C-700	3	4	10	120	43 ^d	
8	Ni-N-C-700	3	4	10	120	13 ^e	
9	MgO	3	4	10	120	NR ^f	
10	NiCl ₂	3	4	10	120	NR ^f	
11	NiCl ₂ , 1,10- phen	3	4	10	120	NR ^f	
12	N-C	3	4	10	120	21	
13	Ni-NC	3	4	10	120	38	
14	Ni-N-C-600	3	4	10	120	82	
15	Ni-N-C-800	3	4	10	120	63	
16	Ni-N-C-700	3	4	10	120	28 ^g	

[a] Reaction conditions: 0.25 mmol 4-nitrochlorobenzene in 5 ml ethanol. [b] isolated yield. [c] 5 ml of H₂O was used as solvent. [d] 5 ml of Ethyl Acetate was used as solvent [e] 5 ml of THF was used as solvent. [f] NR: No Reaction. [g] 4nitrochlorobenzene of hydrogenation in the presence of NaSCN.

shows higher TOF values (8.4 h⁻¹) than the majority of other reported Ni catalysts in the comparative reaction conditions. More importantly, the 100% selectivity of our catalysis hydrogenation reaction is superior to the most of Ni catalysts. Compared with other non-precious metals catalysts, such as Fe and Co, it also shows the comparative catalytic activity and selectivity.

Table 2 Catalytic reduction of nitroarenes into amines by H2 catalyzed by Ni-N-C-700^a



[[]a] Reaction conditions: 0.25 mmol 4-nitrochlorobenzene in 5 ml ethanol, 4 mg catalyst, 120 °C, 3 MPa H₂, 10 h . [b] isolated yield.

ARTICLE

The most outstanding advantage of the heterogeneous catalyst is its capability for easy separation and recycling. The recyclability of Ni-N-C-700 has been evaluated by using 4chloronitrobenzene as a test substrate (Fig. S12). After completion of the reaction, the catalyst was filtered from the reaction and washed with ethyl acetate for the next run. Although, the chemical selectivity is maintained perfect throughout the process, the yield of 4-chloroaniline gradually decreased along with the cycle times. However, the hydrogenation process can complete by extending the reaction time. This result demonstrates that the Ni-N-C-700 catalyst possesses good recyclability. After five times recycles, various experiments have been carried out to examine the recycled catalyst. The SEM images show that the more fragmented is observed compared with the fresh catalyst (Fig. S13a). No any nickel-containing nanoparticles are found in TEM Image (Fig. S13b). HAADF-STEM images reveal that single atom nickel remains in Ni-N-C-700 after cycle reaction (Fig. S13c). EDS mapping result shows that the elements of Ni, N and C are uniformly distributed in the recycled catalyst (Fig. S13d). These results illustrated that the microstructure of catalyst is slightly damaged. However, no aggregation phenomenon was occurred during the reaction. Moreover, we have analysed the leached liquid after the first time reaction by ICP-OES. Trace of nickel (0.8 ppm) can be detected in the reaction solution. In addition, the content of Ni in the five times recycled catalyst was 2.8 wt% **Fig. 3** DFT calculations. The investigated most stable structures of (a-d) nitrobenzen adsorption and (e-h) nitrobenzen and H₂ co-adsorption on Ni-N_x (x = 1-4), as well as the adsorption energy (E_{ads}) and N-O and H-H bond length. The gray, blue, light blue, red, and white balls stand for C, N, Ni, O, and H atoms, respectively. the decrease of the catalysis activity is due to the catalyst structure damage and active species Ni leaching. In order to demonstrate the reaction proceed in a heterogeneous way, the leaching test has been also carried out (Fig. S14). When the catalyst is removed from the reaction, the yield of 4chloroaniline is not increased. When rejoin the Ni-N-C-700 catalyst, the reaction can be accomplished.

3.3 DFT calculations

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To understand the nature of the high hydrogenation of nitroarenes reactivity of atomically dispersed Ni catalyst, density-functional theory (DFT) calculations were performed. As shown in Fig. 3, four Ni-N structures with Ni atoms coordinated with 4 N atoms (Ni-N₄, Ni-N₂₊₂), 3 N atoms (Ni-N₃, Ni-N₃V, Ni-N₃C, Ni-N₃C₂), 2 N atoms (Ni-N₂C₁, Ni-N₂C₂, Ni- N_2 , Ni- N_2V_2) and 1 N atoms (Ni- N_1C_2 , Ni@G) have been considered to represent different Ni-N coordination conditions, where V stands for coordination vacancy. Also, some other typical Ni-N_x (x=1-4) structures are selected, as shown in Fig. S15. To investigate the interaction between nitrobenzene molecule and Ni-N_x, many initial adsorption structures (parallel or vertical to Ni-Nx) were involved into these simulations. Fig. 3a-d show the most stable adsorption structures of nitrobenzene molecule on Ni-N_x and the others are shown in Fig. S16. It is clearly seen that nitrobenzene molecule is adsorbed parallel on the substrates with the AB stacking-like morphology. Also, the adsorption energies (E_{ads}) of nitrobenzene molecule on three substrates are all negative (-0.59 \sim -2.22 eV), suggesting a stable adsorption, and all the N-O bonds are activated with the longer N-O bond length compared to the gas phase (N-O = 1.24

Å), especially for Ni-N₃ substrates. The induced longest $N_{\rm T}Q$ bond indicates the highest catalytic ability. Fig. 384 Coperation most stable co-adsorption configurations of nitrobenzene and H₂ molecules on Ni-N_x. Followed H₂ co-adsorption, the adsorption energies and the length of N-O are slightly increased, promising the subsequent nitrobenzene reduction reaction occur easily. Fig. S17 shows the most stable nitrobenzene and coadsorption structures of nitrobenzene molecules and H₂ on the other optimized Ni-N3 structures. We can find that the Ni-N3 in Fig. 3c possesses the highest catalytic ability according to the lowest adsorption energy and longest N-O bond length, which is consistent with the experimental observations.



To investigate the essential reason for the highest catalytic activity of Ni-N₃, we also plot the charge difference with two kinds of reference, as shown in Fig. 4a-b. From Fig. 4a we can see that most of the charge transferring occurred in H₂ self and small amount on the Ni (yellow part), therefore, we can conclude that the catalyst of Ni-N3 induced polarization of nonpolarized H₂ molecule, which is responsible for the slightly decreased adsorption energy by H₂ co-adsorption, as shown in Fig.3. Furthermore, if we take nitrobenzene and Ni-N₃ (Fig. 4b) as the references, more charges are transferred between N or Ni in Ni-N₃ and N or O in nitrobenzene, which is regarded as the essential reason for the highest catalytic activity of Ni-N₃.



Fig. 4 The charge difference of (a) H_2 vs. Nitrobenen-adsorbed Ni-N₃; (b) nitrobenzen vs. Ni-N₃. Isovalue=0.005 a.u.

4. Conclusions

In summary, atomically dispersed Ni sites on N-doped porous carbon are synthesized by the pyrolysis of coordinatively saturated NiCl₂ with 1,10-phenanthroline using porous MgO template. The structure of as-synthesized Ni-N-C catalysts has been characterized by HAADF-STEM, and the coordination numbers of Ni with N is reduced along with the temperature, as indicated by XAFS and XPS characterization. The Ni-N-C catalyst prepared at 700 °C exhibits high activity for hydrogenation of nitroarenes, great chemoselectivity, and good recyclability. The outstanding catalytic performance originates from the induced change transfer and the active sites are the atomic dispersed single Ni with high Ni-N3 content, which is proven by control experiments and DFT calculations. This study may offer a new strategy for rational design and application of single-atom catalysts in organic molecular transformation reactions.

Author contributions

Fan Yang and Minjian Wang conceived and designed the experiments. Minjian Wang and Bin Yang performed laboratory experiments. Jun Luo, Wei Liu and Yushu Tang carried out TEM. Liqiang Hou, Yun Li, Zihui Li, Bing Zhang, Wang Yang conducted part of the characterization analysis of the material. Ying Wang provided theoretical calculation and discussion. Yongfeng Li and Fan Yang were responsible for planning and supervising the project.

Conflicts of interest

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There are no conflicts to declare.

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Noble-metal-free catalytic hydrogenation of nitroarenes using H_2 as reductant is achieved through the rational design of atomically dispersed Ni sites on N-doped porous carbon. The outstanding activity of the catalyst originates from the atomic dispersion of single Ni active sites with high Ni-N₃ content, proven by control experiments and DFT calculations.