We report the preparation of a porous 3D-foam-structured nitrogen-doped graphene-Ni (NG/NF) catalyst and the evaluation of its performance in the reduction of nitrobenzene (NB) through detailed studies of the kinetics. The NG/NF catalyst showed a significantly higher reaction rate than pure Ni foam (NF). Moreover, the separation of the 3D-foam-structured catalyst from the products was more convenient than that of NG powdered catalysts. The obtained kinetics data fit well to the Langmuir-Hinshelwood model, with an error ratio below 10%. Density functional theory (DFT) calculations indicated that the adsorption of sodium borohydride (NaBH4) on the NG/NF surface was stronger than that of NB, which strongly agreed with the kinetic parameters determined from the Langmuir-Hinshelwood model. The excellent catalytic efficiency of the 3D-foam-structured catalyst combined with the knowledge of the kinetics data make this catalyst promising for application in larger scale nitrobenzene reduction.

Keywords: nitrogen-doped graphene, 3D-foam-structured catalysts, nitrobenzene reduction, Langmuir-Hinshelwood model, density functional theory calculation

Introduction

The reduction of nitrobenzene (NB) to aniline (AB) is an important catalytic reaction because the reaction product is one of the most important intermediates in the production of rubber, coatings, organic pigments, and pesticides. In terms of environmental protection, NB is listed as a priority pollutant in drinking water in many countries. The traditional noncatalytic treatment methods that use Fe as a reducing agent generate large amounts of organic wastewater and toxic solid waste. Therefore, noble metal-based catalysts, such as those containing Au, Pd, and Pt, have been used for the catalytic reduction of nitrobenzene in the aniline production industry.

However, the scalability of the industrial applications of these catalysts is limited due to the limited reserves and high cost of noble metals. Therefore, the development of environmentally friendly, low-cost, and efficient catalysts for this reduction reaction is critical.

Carbon nanomaterials have received intense scientific interest and have found wide application in the fields of biology, energy, and catalysis, among many others. Research on the catalytic use of two-dimensional (2D) graphene has increased significantly over the last 10 years. Tremendous progress has been made on 2D layered materials, and many review articles have focused on the synthetic strategies, physical properties, and applications of such materials. In particular, nitrogen-doped graphene (NG) has been demonstrated as an efficient metal-free catalyst in many industrially important reactions, such as styrene synthesis, cyclohexane oxidation, benzene hydroxylation, and the oxygen reduction reaction. However, the application of powdered 2D graphene catalysts in practical liquid-solid or gas-liquid-solid
multiphase reaction systems has been met with some problems, such as aggregation and the bleeding of the graphene powders.\textsuperscript{25,26} As one technique for improving the properties, structured catalysts have many advantages over conventional pellet or powdered catalysts in terms of the transport characteristics and macro-kinetics of heterogeneous catalytic reactions.\textsuperscript{27} Nickel foam (NF), which can be easily fabricated and is an inexpensive commercial material, exhibits outstanding heat transfer properties, a desirable 3D open-pore structure and suitable mechanical strength and has been widely employed as a substrate template in the preparation of 3D-structured graphene.\textsuperscript{28,29} For example, the combination of 2D

![Figure 1. Schematic illustration of the preparation of NG/NF.](Color figure can be viewed at wileyonlinelibrary.com)

![Figure 2. SEM images of (a) NF and (b) NG/NF; the insets are the corresponding digital photographs of 1 cm × 1 cm × 0.15 cm sections. (c) SEM image corresponding to the elemental mapping images of (d) C, (e) O, and (f) N in NG/NF.](Color figure can be viewed at wileyonlinelibrary.com)
NG and 3D NF has exhibited high performance in electrochemical catalysis. Nevertheless, to the best of our knowledge, the use of 3D-foam-structured nitrogen-doped graphene-Ni (NG/NF) catalysts for the reduction of nitrobenzene has been rarely reported.

Herein, we report the preparation of a 3D-foam-structured NG/NF, its performance as a catalyst for the reduction of nitrobenzene, and detailed studies of the chemical reaction kinetics. The effects of the reaction temperature, superficial area of the catalyst, and concentrations of the initial reactants were investigated. Furthermore, the obtained kinetics data were fit to the Langmuir-Hinshelwood model. Density functional theory (DFT) calculations were also performed to understand the mechanism of the catalytic reaction.

**Experimental Section**

**Materials**

NF with a pore density of 30 ppi was purchased from Shenzhen Hexingchuangda Technology Co. Ltd. Graphene oxide (GO), produced by the modified Hummers method, was obtained from Beijing Chemicals Ltd. Nitrobenzene, sodium borohydride, urea, ethanol, acetone, and hydrochloric acid were purchased from Sigma Aldrich. The reagents were all analytically pure and used without additional purification unless otherwise mentioned. Deionized water was prepared by a Hitech laboratory water purification system, Smart-S30 (Shanghai Hitech Instruments Co. Ltd) and used for all experiments.

**Preparation of NG/NF**

Briefly, raw NF was treated in sequence with acetone and hydrochloric acid for 1 h each to remove contaminants and subsequently washed with ethanol and deionized water. The pretreated NF sheet (2 cm × 1 cm × 0.15 cm) was then soaked in 20 mL of an aqueous GO dispersion (1 mg/mL) under ultrasonic treatment (Kunshan Ultrasonic Instrument Co. Ltd, KQ2200B, 100 W) for 30 min. After that, the GO-coated nickel foam (GO/NF) was removed and dried in air at room temperature for 5 h. For the preparation of NG/NF, the GO/NF was placed in a 50-mL Teflon-lined stainless autoclave with 25 mL of an aqueous urea solution (50 mg/mL) and treated at 180°C for 12 h. The obtained NG/GF was washed...
with water and then dried in air at 60°C for 5 h for further studies of the catalytic performance.

Characterization

Scanning electron microscopy (SEM) imaging and energy-dispersive X-ray (EDX) mapping was performed on a Hitachi S-4700 field emission SEM. Fourier transform infrared (FTIR) spectra were measured on a Thermo Fisher Nicolet 6700 FTIR system. X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Microtech ESCA 2000 instrument using a monochromic Al X-ray source. Raman spectra were collected on a Renishaw in Via Raman spectrometer using a 514-nm wavelength laser. Catalytic reactions were performed at room temperature and monitored by a Shimadzu UV-2600 UV-Vis scanning spectrophotometer.

Hydrogenation of nitrobenzene

In a typical experiment, 3.5 mL of an aqueous solution containing 1 mmol NaBH₄ and 0.01 mmol NB was added to a quartz cuvette (4.5 cm × 1.25 cm × 1.25 cm) along with the NG/NF catalyst (2 cm × 1 cm × 0.15 cm). To investigate the dynamics of the reactions, the NG/NF catalyst was removed from the solution at specified points in the reaction (0–33 min at 3 min intervals), and the absorbance spectrum of the solution was recorded with a UV/vis scanning spectrophotometer. According to the Beer-Lambert law, the absorbance intensity of a chromophore varies linearly with its concentration in a transparent solvent. A set of standard solutions of each chromophore was prepared, and the curve relating the absorbance to the concentration was plotted. The calibration equation shown in Eq. 1 was used to calculate the concentrations of NB and AB at each time point

\[ \text{Abs} = A \times \text{Con} + B \]  

where A and B are standard values obtained from the calibration plot and represent the slope and intercept, respectively. Con and Abs represent the concentration and absorbance of the solute, respectively. In our experiments, the absorbance intensities of peaks at 267 nm and 232 nm were measured to calibrate the NB and AB concentrations, respectively. Bare NF and GO/NF were also used as catalysts in the nitrobenzene reduction studies as control groups for comparison.

DFT simulation

DFT theoretical calculations were performed by the Dmol³ code of Materials Studio 8.0 commercial software. The graphene sheet model used in this study included 110 carbon atoms and 28 hydrogen atoms, which eliminated the edge-hydrogen-atom influence on the whole graphene sheet. The doping energy (\( E_{\text{doping}} \)) was calculated as follows

\[ E_{\text{doping}} = E_{\text{NG}} + E_C - E_{\text{graphene}} - E_N \]  

where \( E_{\text{NG}} \) and \( E_{\text{graphene}} \) are the energies of the optimized structures of nitrogen-doped graphene and intrinsic graphene, respectively. \( E_C \) and \( E_N \) are the total energies of the carbon and nitrogen atoms, respectively.

The adsorption energy (\( E_{\text{ads}} \)) of each reactant was calculated to analyze the relative adsorbability to different materials, which is defined by Eq. 3 as follows

\[ E_{\text{ads}} = E_{\text{total}} - E_{\text{graphene}} - E_{\text{molecule}} \]  

where \( E_{\text{total}} \) is the total energy of the optimized system and \( E_{\text{molecule}} \) is the energy of the adsorbed molecule.

Results and Discussion

The formation of NG/NF is illustrated in Figure 1. On immersion of a section of NF in an aqueous suspension of GO under ultrasonication, the GO sheets rapidly filled the micropores and then coated the NF network. After the removal of water, strong adhesion of the GO to the surface of the nickel metal occurred through van der Waals interactions. During the hydrothermal treatment of GO/NF with urea, the GO sheets were reduced to graphene, and nitrogen was doped into the graphene lattice to form NG/NF composites. As excess GO and urea were used, the surface of NF was estimated to be fully covered with NG owing to the favorable interactions between nickel and GO sheets. The weight ratio of NG to NF was calculated to be 10 wt % based on the weights of the raw NF and the final NG/NF composite. To study the robustness of NG/NF, the release kinetics of NG from NG/NF were investigated by sonication treatment of NG/NF in water. The percentage of NG released from NG/NF was below 1 wt % throughout the sonication treatment (up to 30 min), indicating that the structure of NG/NF was stable (Supporting Information Figure S1).
Photographs of bare NF and NG/NF under visible light, as well as their microstructures observed by SEM, are presented in Figure 2. Bare NF has a metallic luster (inset in Figure 2a) and a typical 3D cross-linked grid structure with pore sizes ranging between 100 and 300 μm (Figure 2a). NG/NF appears dark black (inset in Figure 2b) because the entire NF scaffold is covered with NG sheets (Figure 2b). There are no obvious differences between the SEM images of NF and NG/NF, indicating that the framework of NF was stable during the NG coating process. In the elemental mapping of C, N, and O in a typical SEM image of NG/NF, the signals of C, N, and O, which came from NG, can be clearly observed in the NF network, indicating that the NF was fully covered with NG (Figures 2c–f). The FTIR spectrum of NG/NF (Supporting Information Figure S2) shows the characteristic peaks of C=N and C-N stretching vibrations at 1384 cm\(^{-1}\) and 1165 cm\(^{-1}\), respectively, which also demonstrates the successful deposition of N-doped graphene on the NF.

The presence of NG sheets and their structural composition on NG/NF were further confirmed by Raman spectroscopy and XPS analysis. According to the Raman spectra shown in Figure 3a, the ratio of the D to G bands intensities (I\(_D\)/I\(_G\)) for NG/NF and GO/NF are 1.17 and 0.93, indicating that the degree of defects in NG/NF was higher than that in GO/NF.\(^{37}\) The G band of NG/NF exhibits a blueshift of approximately 10 cm\(^{-1}\) relative to that of GO/NF, which was attributed to the doping of N atoms.\(^{38}\) As shown in Figure 3b, the Raman peaks of NG/NF were deconvoluted into four curves with peaks at 1250 cm\(^{-1}\), 1355 cm\(^{-1}\) (D band), 1450 cm\(^{-1}\) and 1600 cm\(^{-1}\) (G band). The D and G bands reflect the defects in graphene, while the bands at 1250 cm\(^{-1}\) and 1450 cm\(^{-1}\) were attributed to the carbon atoms outside the intrinsic graphene molecules and the change in the graphene structure, respectively. The XPS spectra shown in Figure 3c also demonstrate the successful doping of nitrogen in NG/NF, with an N atomic percentage of 4.3%. The C1s XPS spectrum of GO/NF shown in Figure 3d indicates the presence of three types of carbon bond in GO/NF: graphite sp\(^2\) C (284.71 eV), C-O (286.6 eV), and C = O (289.20 eV). However, four types of carbon bonds, graphite sp\(^2\) C (284.71 eV), N-sp\(^2\) C (286.05 eV), N-sp\(^3\) C (287.55 eV), and C = O (289.20 eV), were observed in the C1s XPS spectrum of NG/NF (Figure 3e), suggesting that nitrogen was doped into the graphene structure. The N1s XPS spectrum of NG/NF shown in Figure 3f indicates the presence of three...
types of C-N bonds, which are pyridinic N (398.85 eV), pyrrolic N (400.2 eV) and graphitic N (401.9 eV), with relative contents of 41.13%, 48.59%, and 10.28%, respectively.

The electron density distribution of graphene is known to become asymmetric after doping nitrogen atoms into the nanocarbon molecules, resulting in a higher positive charge density and spin density on the carbon atoms next to the doped N atoms (Supporting Information Figure S3). The highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of intrinsic graphene, graphitic N, pyridinic N, and pyrrolic N are shown in Supporting Information Figure S4. The main difference between the doped graphene and intrinsic graphene is that the electron distribution in the LUMO became more uniform following the introduction of nitrogen, which results in a better electron accepting ability of the nitrogen-doped graphene. In our experiments, the doping energies (E_{doping}) of graphitic N, pyridinic N and pyrrolic N were calculated as 3.54, 2.929 and 2.316 eV, respectively (Supporting Information Table S1). These theoretically calculated results suggest that pyrrolic N exhibits the lowest doping energy, which means that this type of N-C bond is the most likely to be introduced into the graphene units. These results are consistent with the XPS analysis (Figure 3f).

The performance of NG/NF as a catalyst for the reduction of NB is presented in Figure 4. As shown in the absorbance spectra given in Figure 4a, the intensity of the NB absorbance peak at 267 nm rapidly decreased due to the reaction of NB with NaBH₄ in the solution. An absorbance peak at 232 nm, which is the characteristic absorbance peak of AB based on the absorbance spectrum of AB shown in Supporting Information Figure S5, grew as the reaction continued, indicating the formation of AB from the reduction of NB. The presence of an isosbestic point at 243 nm illustrates that no by-products formed during the reaction. The reaction was continuously monitored for over 30 min, and Figure 4b gives the curve of ln (C / C₀) as a function of the reaction time, where C₀ is the initial concentration of NB and C represents the concentration of NB at each time point. The results given in Figure 4b show that the reduction of NB to AB by NaBH₄ in the presence of NG/NF as the catalyst followed pseudofirst-order kinetics. However, when no catalyst was used, very little NB was reduced over 2 h, even when excess NaBH₄ was added into the NB solution (Supporting Information Figure S6a). When GO/NF was used as the catalyst, a decrease in the absorbance intensity of NB in the solution was observed, but the absorbance peak corresponding to AB did not appear (Supporting Information Figure S6b), suggesting that the decrease in the NB peak was caused by the physical adsorption of NB to the graphene oxide. Therefore, the nitrogen doping of NG/NF was the key factor in the catalytic reduction of NB to AB by NaBH₄. The reusability of the catalyst was also investigated, and the activity of NG/NF decreased by no more than 20% after eight cycles (Supporting Information Figure S7).

The catalytic reduction of NB by NG/NF at various reaction temperatures (17, 30, 40, and 49°C) was further investigated, and the corresponding plots of ln (C / C₀) vs. time (t) are shown in Figure 5a. As the reaction of NB to AB exhibited pseudofirst-order kinetics in our experiments, the apparent kinetic rate constant (k_{app}) for the reaction was calculated from the following Eq. 4. The plot of ln (k_{app}) vs. the inverse of temperature (K⁻¹) is presented in Figure 5b.

\[
\ln \left( \frac{C}{C_0} \right) = k_{app} \cdot t
\]  

(4)

In this equation, C₀ and C, represent the initial concentration of NB and the concentration of NB at a given time point in the reaction, respectively; k_{app} is the apparent kinetic rate constant; and t is the reaction time.

The reaction system exhibited a strong dependence of k_{app} on the temperature, corresponding to a gradual increase in the solubility as the temperature increased in the range of 17–49°C. These experimental results can be explained by the collision theory. With increasing reaction temperature, the molecular movement becomes more violent, resulting in a greater chance of collision, which then causes an increase in the apparent reaction rate. The apparent activation energy (E_a) was calculated to be 30.50 kJ/mol according to the Arrhenius equation given in Eq. 5.

\[
\ln k_{app} = \ln A - \frac{E_a}{RT}
\]  

(5)

In this equation, E_a is the apparent activation energy, A is a pre-exponential factor, and R is the general gas constant (R = 8.314 J/[K·mol]).

As the catalytic reduction of NB to AB is a type of surface transfer reaction and requires coadsorption of the reactants to the surface of the catalyst, the reaction parameters, such as the superficial area of the catalyst and the initial concentrations of NB (C_{NB}) and NaBH₄ (C_{BH4}), play important roles in determining the value of k_{app}. In this work, the effects of such
reaction parameters were evaluated through single factor experiments at room temperature. For NG/NF, the superficial area was directly proportional to the mass of NG/NF. Figure 6a shows the plot of $k_{\text{app}}$ as a function of the mass of the NG/NF catalyst, in which the value of $k_{\text{app}}$ increases with increasing mass of NG/NF. In that experiment, the values of $C_{\text{NB}}$ and $C_{\text{BH}_4^2}$ were 9.788 $\times$ 10$^{-5}$ mol/L and 0.0132 mol/L, respectively. Figures 6b, c show the dependence of $k_{\text{app}}$ on $C_{\text{NB}}$ and $C_{\text{BH}_4^2}$, respectively. Under the conditions of constant $C_{\text{BH}_4^2}$ (0.0132 mol/L) and $m_{\text{NG/NF}}$ (20 mg), $k_{\text{app}}$ first increased and then decreased with increasing $C_{\text{NB}}$. In contrast, under constant $C_{\text{NB}}$ (9.788 $\times$ 10$^{-5}$ mol/L) and $m_{\text{NG/NF}}$ (20 mg), $k_{\text{app}}$ monotonically decreased with increasing $C_{\text{NB}}$. These results suggest that during the reaction, the borohydride ions first adsorbed to the surface of NG and then transferred hydrogen to form a surface-bound hydrogen species, which was followed by the adsorption of NB molecules to the catalyst. This mechanism agrees with previous reports on NB reduction by NaBH$_4$ in the presence of metal catalysts.$^{43}$

The above experimental results were then fitted by the Langmuir-Hinshelwood (L-H) model$^{44}$

$$\frac{dC_{\text{NB}}}{dt} = -k \cdot S \cdot \theta_{\text{NB}} \cdot \theta_{\text{BH}_4^2}$$

(6)

In this equation, $k$ is the intrinsic rate constant, and $\theta_{\text{NB}}$ and $\theta_{\text{BH}_4^2}$ are the surface coverages of NB and BH$_4^2$ on NG/NF, respectively, which can be modeled by Langmuir isotherms as follows

$$\theta_{\text{NB}} = \frac{(K_{\text{NB}} \cdot C_{\text{NB}})^n}{1 + (K_{\text{NB}} \cdot C_{\text{NB}})^n + (K_{\text{BH}_4^2} \cdot C_{\text{BH}_4^2})^m}$$

$$\theta_{\text{BH}_4^2} = \frac{(K_{\text{BH}_4^2} \cdot C_{\text{BH}_4^2})^m}{1 + (K_{\text{NB}} \cdot C_{\text{NB}})^n + (K_{\text{BH}_4^2} \cdot C_{\text{BH}_4^2})^m}$$

(7)

where $K_{\text{NB}}$ and $K_{\text{BH}_4^2}$ are the adsorption constants of NB and BH$_4^2$, respectively, and $C_{\text{NB}}$ and $C_{\text{BH}_4^2}$ are their corresponding concentrations in solution.

Therefore, $k_{\text{app}}$ can be derived from the substitution of Eq. 7 into Eq. 6 and finally expressed as follows

$$k_{\text{app}} = \frac{k \cdot S \cdot K_{\text{NB}}^n \cdot C_{\text{NB}}^{n-1} \cdot K_{\text{BH}_4^2}^m \cdot C_{\text{BH}_4^2}^m}{(1 + (K_{\text{NB}} \cdot C_{\text{NB}})^n + (K_{\text{BH}_4^2} \cdot C_{\text{BH}_4^2})^m)^2}$$

(8)

The parameters in the model were calculated, and the results are listed in Supporting Information Table S2. The plot of the $k_{\text{app}}$ values predicted by the L-H model vs. the experimental values of $k_{\text{app}}$ is presented in Figure 6d. The deviation between the two groups was less than 10%, indicating that the experimental kinetics data fit well to the L-H model.

Furthermore, the 3D plot of $k_{\text{app}}$ vs. $C_{\text{NB}}$ and $C_{\text{BH}_4^2}$ obtained from the calculated L-H equation (Eq. 9) is shown in Figure 7a. The calculated L-H equation is expressed as follows

$$k_{\text{app}} = \frac{0.2 \cdot C_{\text{NB}}^{-0.5} \cdot C_{\text{BH}_4^2}}{(1 + 4.58 \cdot C_{\text{NB}}^{-0.5} + 23.94 \cdot C_{\text{BH}_4^2})^2}$$

(9)

which then transforms to
According to Eq. 10, \( k_{\text{app}} \) and \( C_{\text{NB}} \) are negatively correlated, that is, when the concentration of NB increases, the value of \( k_{\text{app}} \) gradually decreases. This trend agrees well with the experimental results shown in Figure 6b. The relationship between \( k_{\text{app}} \) and \( C_{\text{BH}_4} \) can be described by a basic quadratic equation. Therefore, \( k_{\text{app}} \) first increased to a maximum value and then decreased with increasing \( C_{\text{BH}_4} \). From the enlarged plot shown in Figure 7b, the optimized concentration of NaBH\(_4\) for the reduction of low concentrations of NB in the above catalytic reaction system was identified as 0.025 mol/L.

DFT calculations were then performed to further understand the catalytic reduction of NB to AB with NG/NF as the catalyst. The graphene sheet has a perfectly planar structure before adsorbing a NB molecule (Figures 8a, b). However, both graphene and NG exhibit varying degrees of distortion on adsorption of the NB molecule via close interaction with a carbon atom near the edge (intrinsc graphene) or next to a doped nitrogen atom (NG) (Figures 8c–f). The distance between the C-O bond of the NB molecule and the NG sheet was approximately 5 Å. The adsorption energy of NB on intrinsic graphene, graphitic N, pyridinic N and pyrrolic N was calculated as 0.182, 0.195, 0.189, and 0.265 eV, respectively (Supporting Information Table S1). The adsorption energies of NaBH\(_4\) and NB on the graphitic N-doped graphene was obtained, and the ratio of their energies (\( E_{\text{ads}} \)–NB : \( E_{\text{ads}} \)–NaBH\(_4\) = 1.145) matched well to the ratio of \( K_{\text{NB}} \) and \( K_{\text{NaBH}_4} \) (\( K_{\text{NB}} : K_{\text{NaBH}_4} = 1.14 \)) obtained by fitting the experimental data to the L-H model. These results also demonstrate the prior adsorption of NaBH\(_4\) in the reaction process. \(^{11,41} \)

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