

Synthesis of Nickel Nanoparticles with N-Doped Graphene Shells for Catalytic Reduction Reactions

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The synthesis of novel nanoparticles is of general importance for the development of efficient heterogeneous catalysts. Herein, the preparation of carbon-supported nickel-based nanoparticles (NPs), modified by nitrogen-doped graphene layers, is reported for the first time. The resulting materials were characterized in detail by TEM, X-ray photoelectron spectroscopy (XPS), XRD, elemental analysis (EA), electron paramagnetic resonance (EPR), temperature-programmed reduction (TPR), BET, and Raman analysis. Initial catalytic tests revealed the potential of this class of compounds in hydrogenation reactions.

The synthesis of novel catalysts provides innovation for the chemical- and life-science industries because catalysts are able to specifically control both the selectivity and reaction rate of many molecular transformations.^[1] The synthesis of novel materials provides the basis for innovation in heterogeneous catalysis, which is mainly applied for the production of petrochemicals as well as bulk and fine chemicals. Advantageously, heterogeneous catalysts are easily recycled by filtration and reutilized. Notably, in the last decades especially, metal nanoparticles (NPs) dispersed on different supports have found increasing application as catalysts.^[2] In general, these nanoparticles are prepared by a range of different procedures, namely precipitation, calcination, impregnation, ion exchange, hydrothermal transformations, or vapor deposition.^[3] In addition, the past decades have witnessed an explosion in new methods for the synthesis of metal nanoparticles with controlled composition, size, shape, and structure.^[4] Herein, we present the synthesis of novel NPs covered by nitrogen-doped graphene sheets (NGrs) from well-defined molecular nickel complexes. Apart from the well-known Raney nickel,^[5] nickel nanoparticles have also found widespread interest for several catalytic appli-

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[c] Dr. S. Bachmann, Dr. M. Scalone F. Hoffmann-La Roche AG Process Research and Development, CoE Catalysis 4070 Basel (Switzerland) cations,^[6] such as the hydration of carbon dioxide,^[7] dehydrogenation of ammonium borane,^[8] and transfer hydrogenation.^[9] Recently, we demonstrated that core–shell structured nanocomposites based on iron and cobalt constitute highly selective catalysts for the hydrogenation of nitroarenes,^[10] reductive amination,^[11] the synthesis of nitriles,^[12] as well as oxidation reactions of alcohols.^[13] Notably, all active NPs, for example, Fe₂O₃/NGr@C or Co-Co₃O₄/NGr@C, are encapsulated by a nitrogen-enriched graphene-layer matrix. Based on this work and our general interest in non-noble-metal catalysis, we envisioned the synthesis of related Ni-NiO/NGr@C materials. In this protocol, we demonstrate the preparation of this class of compounds by impregnation of carbon (Vulcan[®] XC72R) with a defined nickel-phenanthroline complex and subsequent pyrolysis (Figure 1). The resulting material was characterized in detail by



Figure 1. Schematic representation of the Ni-NiO/NGr@C catalyst.

several analytical techniques [TEM, BET, X-ray photoelectron spectroscopy (XPS), XRD, electron paramagnetic resonance (EPR), elemental analysis (EA), and Raman spectroscopy] and its catalytic activity was investigated in the reductive amination of acetophenone and in the hydrogenation of nitroarenes.

The preparation was carried out by mixing Ni(OAc)₂ (1.5 or 3 wt%) with 2 equivalents of 1,10-phenanthroline (phen) in absolute ethanol at 70 °C. After stirring the solution for 1 h, the complex formed in situ was impregnated on Vulcan[®] XC72R.^[14] This type of carbon black represents an attractive support material for the synthesis of redox catalysts because of its thermal stability. After removal of the solvent, the remaining material was pyrolyzed under argon at 600–800 °C. In addition to commercial Vulcan[®] XC72R, activated carbon (pretreatment with 30% hydrogen peroxide), Al₂O₃ (alpha phase), TiO₂ (mixture of rutile and anatase, < 100 nm particle size), and CeO₂ (powder, trace-metal basis) were used as the support. To increase the concentration of the nitrogen species in the NGrs, pyrolysis was also performed under an ammonia atmosphere.

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Following the above-described procedure approximately 20 potential Ni catalysts were prepared and tested for the reductive amination of acetophenone and *N*-benzyl-ethyl amine and also for the hydrogenation of aromatic nitro compounds. The most active catalyst (Ni-NiO/NGr@C-800) was prepared by pyrolysis of the in situ formed Ni/phen complex at 800 °C. For a better understanding of the composition and the structure of this material, it was fully characterized by TGA, XRD, XPS, TEM, Raman spectroscopy, EPR, BET and TPR. The sample composition of Ni-NiO/NGr@C-800 was determined by elemental analysis in weight percentage of Ni (3.17%), N (2.31%), C (81.8%), and H (0.32%).

The results of the thermogravimetric analysis of the unpyrolyzed Ni catalyst on Vulcan[®] XC72R are displayed in Figure S1 in the Supporting Information. Apparently, the formation of nickel nanoparticles and the accompanied carbonization proceeds in a multistage fashion. Initial dehydration of the material is indicated by the broad peak between 100 and 250 °C of the differential scanning calorimetry (DSC) graphs. The subsequent exothermic process at 271 °C is assigned to the loss of excess 1,10-phenanthroline as well as the initial decomposition of the ligated nickel acetate. The third exothermic step, ranging from 450 to 500 °C, is accompanied by a significant loss of mass (15%) and may be assigned to the decomposition of the ligated nickel acetate, which culminates in the formation of NiO and metallic nickel as well as the generation of the Ndoped graphene layers.

The powder XRD pattern of the prepared material is displayed in Figure S2. In accordance with existing data (JCPDS file No. 65-2865), metallic nickel was detected by the characteristic peaks at Bragg's angle 44, 52, and 76°. In contrast to the TEM measurements (see below), surprisingly no nickel oxide species could be detected. Apparently, the NiO concentration is very low. Notably, the broad peak at approximately 25° arises from the amorphous structure of the carbonaceous matrix.^[15]

To elucidate the detailed structure further, the binding energy (BE) of the surface species was measured by XPS. The high-resolution spectra of N1s exhibits three peaks that are characteristic for nitrogen-doped graphene. The detection of signals for pyridinic N (398.8 eV), pyrrolic N (400.5 eV), and quaternary ammonium indicates the incorporation of different nitrogen species into the carbon matrix (Figure 2A). Furthermore, the C1s spectrum confirms the presence of various carbon species. For example, the sharp C1s peak at 284.2 eV indicates characteristic sp² carbon atoms (Figure 2B). Besides, smaller peaks at higher energy refer to carbon species with triple bonds and the existence of oxygen-containing groups such as C–OH (285.2 eV), carbonyls (286.1 eV), and carboxylates (289.7 eV) (Figure 2B).^[16]

The spectrum of Ni2p shows two characteristic peaks with the corresponding satellites arising from NiO $(2p_{\frac{1}{2}}: 855.1 \text{ and} 861.8 \text{ eV}, 2p_{\frac{1}{2}}: 872.5 \text{ and } 879.2 \text{ eV}, Figure 3 A}).^{[17]}$ The presence of nickel oxide species is proven by a broad peak at 532.7 eV in the high-resolution O1s spectra. This peak might also be assigned to adsorbed oxygen at the surface (Figure 3 B).^[18]



Figure 2. High-resolution XPS spectra of A) N1s and B) C1s of Ni-NiO/ NGr@C-800.

Transmission electron microscopy (TEM) measurements of Ni-NiO/NGr@C-800 were deployed to elucidate the size of the formed nickel nanoparticles and the texture of the surface of the functionalized carbonaceous material. Additional energy dispersive X-ray analysis (EDX) gave insight into the chemical composition of the surface. As shown in Figure 3 the resulting nickel particles are spread over the surface of the carbon support. They are of 10–50 nm size and consist mostly of a metallic nickel core irregularly covered with nickel oxide, which is confirmed by further dispersive X-ray analysis (Figure 4).

Interestingly, the corresponding bright field contrast imaging shows that the nickel NPs are clearly encapsulated in a carbonlayer matrix that results from decomposition of the 1,10-phenanthroline ligand (Figure 5).

Additional structural information of the carbon support and the formed NGrs is provided by the Raman spectra. The amorphous character of the surface is underlined by the appearance of the two peaks *G* (graphitic or graphene) and *D* (disordered or defect) at 1589 and 1339 cm⁻¹ for visible excitation (Figure S3). Both peaks arise from sp² carbon bonds and correspond to bond-stretching modes. More specifically, the G-band refers to planar sp²-carbon modifications and the D-band is peculiar for the "breathing" mode originating from sp²-carbon rings.^[19] Similar to the XRD analysis, no signals corresponding to the presence of nickel oxide were detected. This again con-





Figure 3. High-resolution XPS spectra of A) Ni 2p and B) O 1s of Ni-NiO/ NGr@C-800.

firms our assumption, that the major species of the nickel particles is metallic Ni^0 .



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Figure 5. A) High-angle annular dark-field (HAADF); B) Bright-field (BF) contrast imaging of Ni-NiO/NGr@C-800. Scale bar = 2 nm.

Another powerful tool for the elucidation of the nature of the catalytic material is electron paramagnetic resonance spectroscopy (EPR). The spectrum reveals the typical ferromagnetic character of bulk metal phase (g=2.21) according to the isotropic symmetrical shape (Figure S4).

The determination of the specific surface of the Ni-NiO/ NGr@C-800 material was realized through BET measurements. According to the IUPAC classification, the resulting isotherms resemble an IV isotherm (Figure S5).^[20] The isotherm shows a hysteresis between the adsorption and desorption curves and is typical for mesoporous materials^[21] and also indicates the formation of a gaseous monolayer. The BET surface of Ni-NiO/NGR@C was calculated to be 76.5 m²g⁻¹, the average pore diameter amounted to 9.4 nm, and a single-point total pore



Figure 4. EDX mapping of Ni-NiO/NGr@C-800: A) Metallic nickel core; B) Nickel oxide layer.

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volume of 0.18 cm³g⁻¹ was obtained. In comparison, the surface of pure carbon (Vulcan[®] XC72R) features a surface area of 226.3 m²g⁻¹, an average pore diameter of 5.4 nm and a single point total pore volume of 0.30 cm³g⁻¹. The diminished surface and pore diameter as well as the pore volume of the metal-based material may arise from the fact that the pores are filled with Ni nanoparticles and covered by a carbon-layer matrix.

Temperature-programmed reduction (TPR) has been used to understand the reducibility of the implicated Ni species. The reduction profile shows a peak at 586.5 °C, which seems to be very high compared to other reports (Figure S6).^[22] Usually, a peak at approximately 450 °C is observed for pure nickel oxide and for supported nickel at slightly elevated temperature. The relatively high-temperature measured in this case may be assigned to nickel species strongly attached to the support and/or the hydrogen spillover. Another reason for a high-temperature peak could also be low nickel loading, which is peculiar for distinct contact between support and metal species. Calculations, based on the consumed hydrogen amount, implicate the heterogeneous material to consist of >90% reducible nickel species. This stands in contradiction to XRD measurements, which revealed the nanoparticles to be mainly of metallic nature. One obvious reason for this high hydrogen turnover may be assigned to hydrogen spillover. The temperature-programmed desorption of hydrogen (H₂-TPD) shows two peaks (Figure S6). Only materials containing a metal phase show the appearance of two peaks, whereas the peak at high temperature is attributed to changes of functionalities of the support (801 °C). The peak at lower temperature refers to the existence of a metallic portion.^[22]

The direct reductive amination reaction is a straightforward method to synthesize amines, without the necessity of prior isolation of the intermediate imine.^[23] This process allows for the formation of several substituted amines starting from easily available carbonyl compounds. Usually, this procedure is accomplished in a one-pot reaction, wherein the formed intermediates such as imines, enamines, or iminium cations are subsequently reduced. The initial experiments were performed on the benchmark reaction shown in Table 1. The various catalysts were tested for reductive amination under previously optimized conditions.^[11a,b] To exclude the activity of the support, the latter was tested separately (Table 1, entry 8). Compared to the known cobalt catalyst (Co-Co₃O₄/NGr@C), the nickel analogues prepared under the same conditions display similar activity (Table 1, entries 1 and 2). Catalysts with lower metal loading or those pyrolyzed at lower temperature showed slightly reduced activity (Table 1, entries 3, 4). Furthermore, the use of oxidatively pretreated carbon does not increase the activity (Table 1, entry 5). No, or low activity was observed for the catalyst prepared in the presence of ammonia and for the homogeneous nickel phenanthroline complex fixed on Vulcan® XC72R without pyrolysis (Table 1, entries 6 and 7).

In addition, this novel Ni catalyst was also active in the hydrogenation of nitroarenes to give the corresponding anilines. The reduction of nitrobenzene to aniline was investigated and the findings are summarized in Table 2.



[a] isolated yields. [b] Pyrolysis at 600 °C. [c] 1.5 wt%. [d] Carbon previously treated with H_2O_2 (aq., 30%). [e] Pyrolysis in the presence of ammonia. [f] Homogeneous complex on Vulcan[®] XC72R.



The employed reaction conditions were similar to those reported in our previous publications.^[10a] The catalytic tests clearly show that prolonged reaction time (8 h) is beneficial for the aniline yield (Table 2, entries 3 and 6). Furthermore, a higher Ni loading of 5 mol% improved the formation of aniline. Finally, addition of an equivalent of an organic base, such as Et₃N, further increased the efficiency of the system (Table 2, entries 2 and 3, 5, and 6) and the desired product was obtained in quantitative yield. Then, with these optimal conditions in hand (Table 2, entry 6), the scope of the reaction was investigated with seven functionalized nitroarenes (Scheme 1). In all cases, this catalytic system showed complete conversion and high selectivities for the reduction of the nitro group, even in the presence of other sensitive reducible functional groups. In fact, carbonyl (5 b) and conjugated olefin (5 c) groups were successfully tolerated. In the case of substrate 4g, the yield is due to the formation of 4-vinylaniline as the side product. Moreover, for halogen-containing substrates (5d) and ether-containing molecules (5 e), no dehalogenation and no C-O bond cleavage occurred, respectively. In addition, this catalytic protocol allows for the selective hydrogenation of nitropyridine affording the corresponding heteroaryl amine (5 f) in good yield. Finally, for



Scheme 1. Substrate scope for the hydrogenation of substituted nitroarenes. [a] GC yield with hexadecane as the internal standard; [b] reaction time was 16 h; [c] small amounts (<5%) of 4-vinylaniline were detected.

the reduction of 2,4-dinitrotoluene (4h) a prolonged reaction time is beneficial to obtain the desired product (5h) in high yield.

In conclusion, a novel mesoporous material prepared by impregnation of Vulcan[®] XC72R with an in situ generated nickel acetate/1,10-phenanthroline complex and subsequent pyrolysis of the adsorbed complex is presented. The character and chemical composition of the heterogeneous material was elucidated by the utilization of several analytic techniques. It was shown that the supported material mainly consists of bulk metallic nickel nanoparticles with NiO fractions on its surface. Those nickel-based particles are spread over the support and partly occupy the pores of the support and are also covered with an N-doped graphene-layer matrix. Initial activity tests revealed applicability in different hydrogenation reactions with molecular hydrogen. More specifically, reductive amination reactions and hydrogenation of aromatic nitro compounds proceeded with high yield and selectivity.

Experimental Section

Preparation of the catalytically active material

Vulcan[®] XC72R-supported nickel-based materials were prepared by the impregnation method as previously reported.^[10,11] Nickel acetate tetrahydrate (1.0 equiv., Aldrich 98%) was dissolved in absolute ethanol (20 mL). Afterwards, 1,10-phenanthroline (2.0 equiv., Aldrich \geq 99%) was added and the resulting solution was stirred for 1 h at 60°C. The mixture was cooled to RT, Vulcan[®] XC72R (CABOT Corporation) was added and the resulting suspension was stirred overnight at RT. Afterwards, the solvent was evaporated carefully under reduced pressure to dryness and the obtained solid was dried overnight in vacuo. To obtain the final nitrogen-doped graphene-coated nickel nanoparticles on carbon, the material was grinded and pyrolyzed in a crucible with a lid at 800 or 600°C for 2 h under Ar atmosphere.

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