

A study concerning the pretreatment of CNTs and its influence on the performance of NiB/CNTs amorphous catalyst

CHANG YUAN HU^{1,2}, FENG YI LI^{1*}, LI HUA and RONG BIN ZHANG¹

¹*Department of Chemistry, Nanchang University, Nanchang, Jiangxi 330047, P. R. and* ²*Jiangxi Key Laboratory of Nationals Surface Engineering, Jiangxi Science and Technology Normal University, P.O. Box 224, Nanchang 330013, P.R. China (e-mail: fy-li@hotmail.com)*

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Abstract: As prepared carbon nanotubes were pretreated with nitric acid (CNTs-HNO₃) or ammonia (CNTs-NH₃). Fourier transform infrared spectroscopy (FTIR) measurements showed that the surface of the nanotubes was functionalized with carboxylic and hydroxyl functional groups after the acid treatment and that basic groups containing nitrogen, such as N–H and C–N, were introduced to the surface of the nanotubes after the ammonia treatment. X-Ray diffraction analysis implied that the nickel residue in the CNTs was effectively removed by acid treatment. However, the nickel residue was only partially eliminated by ammonia pretreatment. NiB amorphous catalysts supported on CNTs-HNO₃ and CNTs-NH₃ were prepared by the impregnation–chemical reduction method and characterized by transmission electron microscopy (TEM), as well as inductively coupled plasma (ICP) spectroscopy and studied in the selective hydrogenation of acetylene. TEM measurements showed that a high density NiB particles of about 9 nm were homogeneously dispersed on the CNTs-NH₃. However, NiB particles (13–23 nm) with a mean size of 16 nm were scattered on the CNTs-HNO₃. As a result, the activity and selectivity of NiB/CNTs-NH₃ were higher than those of NiB/CNTs-HNO₃ in the selective hydrogenation of acetylene.

Keywords: CNTs, pretreatment, NiB amorphous catalyst, acetylene selective hydrogenation, ammonia.

INTRODUCTION

Carbon nanotubes as one-dimensional materials, due to their extraordinary mechanical, electronic and hydrogen storage properties, have attracted considerable attention in recent years.^{1,2} Attaching nanoparticles to nanotubes and the side-walls of nanotubes is of interest and significant for obtaining nanotubes/nanoparticles composite materials with useful properties. For example, metal-filled CNTs are especially promising for application as heterogeneous catalyst.^{3,4}

* Corresponding author.

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Amorphous alloy materials possessing more surface atoms and a high concentration of highly coordinated unsaturated sites, on the other hand, have attracted extensive interest since the 1980s for various applications, particularly for hydrogenation reactions, because of their higher activity, better selectivity, and stronger resistance to sulfur in comparison with the corresponding crystalline metal catalysts.^{5,6} It is to be expected that a combination of carbon nanotubes with NiB amorphous alloy may be versatile catalytic materials in various hydrogenation reactions.

However, the inert pristine surface of CNTs makes them a difficult substrate on which to attach particles. Thus, pretreatment of as prepared CNTs is necessary for producing hybrid materials containing nanotubes. A large number of pretreatment methods have been reported, but refluxing in nitric acid has probably been the most employed treatment.⁷⁻⁹ Recently, Gao *et al.*^{10,11} applied a novel effective treatment of CNTs in ammonia to modify the nanotubes. Compared with refluxing in nitric acid, the gas treatment may be more convenient and less time-consuming. Although the above mentioned methods were reported in the literature a comparative study of these treatments, especially the influence of CNTs pretreatments on the performance of NiB/CNTs catalysts, remains to be investigated. In this study, CNTs treated with nitric acid or ammonia and the NiB amorphous alloy supported on the pretreated CNTs were characterized by FTIR, XRD, ICP, BET and TEM. Also, the performance of the NiB/CNTs catalysts was determined in the selective hydrogenation of acetylene.

EXPERIMENTAL

Pretreatment of CNTs and preparation of NiB/CNTs

The CNTs were prepared by chemical vapor deposition (CVD) of methane using a Ni-Cu-Al catalyst.¹² The pretreatment of CNTs was as follows:

Acid treatment (CNTs-HNO₃): the as-prepared CNTs were refluxed for 2 h in 2 M KOH solution (containing 0.5 wt% sodium dodecyl sulfate (SDS: CH₃(CH₂)₁₁OSO₃Na)),¹³ and then the resulting dispersion was filtered and rinsed with deionised water. Thereafter, the sample was refluxed in concentrated nitric acid for 4 h and functionalised in aqueous solution of a mixture of H₂SO₄-HNO₃ (2M : 4M) for 4 h. **Ammonia treatment (CNTs-NH₃):** the CNTs were placed in a boat-shaped tube and heated to 873 K in a laboratory furnace under a flow of ammonia. After holding at this temperature for 3 h, the samples were cooled to room temperature under a flow of ammonia.^{10,11}

The desired amount of CNTs-HNO₃ and CNTs-NH₃ were impregnated with an ethanolic solution of 0.1 M NiCl₂·6H₂O overnight (the Ni/CNTs weight ratio was 1/3). The mixture was reduced by adding dropwise over 30 min a 3M aqueous solution of KBH₄ (the Ni/B mole ratio was 1/3) under vigorous stirring at room temperature. The formed black precipitate was filtered off, thoroughly soaked with distilled water, rinsed with ethanol and then dried at room temperature. The corresponding catalysts were labeled as NiB/CNTs-HNO₃ and NiB/CNTs-NH₃.

Characterization of the samples

The spectroscopic measurements were carried out in the absorbance mode using a Bomem (Spectrum one, FT-IR Perkin-Elmer). The composition of the catalysts was analyzed by inductively coupled plasma (ICP) spectroscopy. The morphology and the particle size of the catalysts were determined by transmission electron microscopy (H-600, Hitachi, Japan). The specific surface areas of

the samples were characterized by nitrogen absorption at 77 K. The XRD patterns of the samples were obtained *via* a Rigaku Automatic diffractometer (D/MAX-RA, Japan).

Selective hydrogenation

To perform acetylene selective hydrogenation, nitrogen containing 2 % (v/v) acetylene and 4 % (v/v) hydrogen was allowed to flow through a reactor. The catalysts (100 mg) were reduced *in situ* at 493K with H₂ for 30 min before the reaction.

The flow rate of the reactant mixture was 50 ml/min during the reaction. The reactant and product were analyzed with an online gas chromatograph equipped with a TCD, using a porapak N column. The acetylene conversion, *X*, and ethylene selectivity, *S*, were calculated as follows:

$$X / \% = (c_{C_2H_2}^0 - c_{C_2H_2}) / c_{C_2H_2}^0$$

$$S_{C_2H_4} / \% = c_{C_2H_4} / (c_{C_2H_2}^0 - c_{C_2H_2})$$

where $c_{C_2H_2}^0$ is the initial concentration of acetylene in the reactant mixture and $c_{C_2H_2}$ and $c_{C_2H_4}$ are the concentration of acetylene and ethylene in the product, respectively.

RESULTS AND DISCUSSION

FTIR measurement of the CNTs

The infrared spectra (Fig. 1) indicate that the absorptions at 1720, 3400, and 1626 cm⁻¹ are evidently related to the presence of carboxylic and hydroxyl groups, resulting from oxidation of nitric acid.⁸ They indicate that treatment with nitric acid can modify the surface of CNTs with functional groups, which is significant as they provide specific sites for the nucleation of metal particles. On the other hand, NH₃ treatment of CNTs generates basic nitrogen-containing groups on the nanotubes.⁹ Compared with those of the stretching vibrations of O–H groups, the broad, rough and lower shift absorptions are distinct characteristics of N–H vibrations originating from the dipole of nitrogen. As shown in Fig. 1b, the appearances of bands of 3413, 1630 and 1400 cm⁻¹ arise from the stretching vibrations of N–H, the bending vibration of N–H and the stretching vibrations of C–N, respectively.^{10,11,14} Due to the hydrophilicity of these groups, the relatively easy dispersion of the CNTs in hydrophilic media such as ethanol, is enabled.

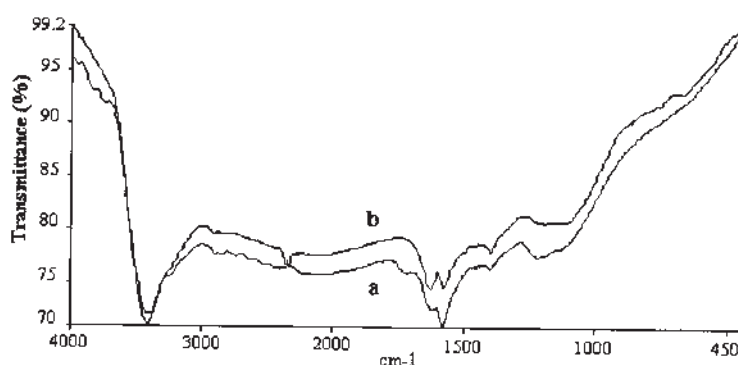


Fig. 1. FTIR spectra
(a) CNTs–HNO₃,
(b) CNTs–NH₃.

TABLE I. Some characteristics of the samples

Sample	Ni-loading/wt%	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	Composition mole ratio	Particle size nm^{D}
NiB/CNTs-NH ₃	15.75	81.7 ^A	Ni _{80,91} B _{19,19}	9
NiB/CNTs-HNO ₃	15.82	85.4 ^A	Ni _{80,65} B _{19,35}	16

^{A,B,C} The surface area of NiB/CNTs, pretreated CNTs, as-grown CNTs, respectively. ^DObtained by TEM.

XRD measurement of the samples

The diffraction peak around 26.5° observed in Fig. 2 for all samples can be attributed to the hexagonal graphite structure (002).^{15,16} The presence of cubic nickel peaks near 45° and 52° in the as-grown CNTs profile can be assigned to the Ni residue from the Ni–Cu–Al catalyst. For CNTs-HNO₃, as shown in Fig. 2c, the charac-

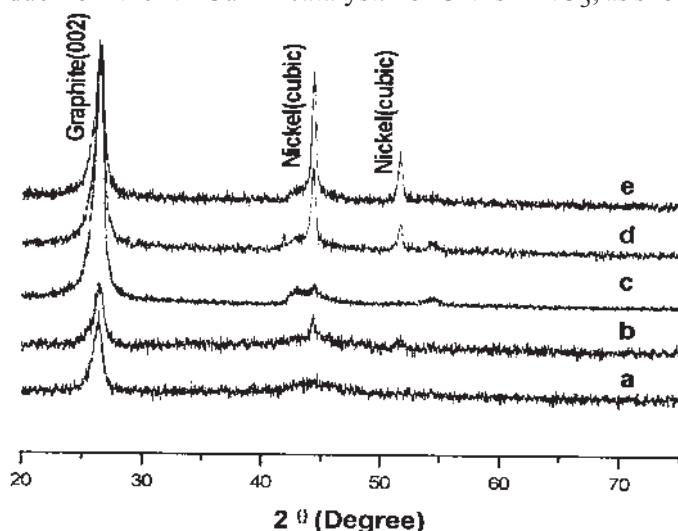


Fig. 2. Powder X-ray diffraction patterns of the samples. a: NiB/CNTs-HNO₃, b: NiB/CNTs-NH₃, c: CNTs-HNO₃, d: CNTs-NH₃, e: as-grown CNTs.

teristic peaks of cubic nickel are almost absent, which indicates that the acid pretreatment removes the metal catalyst effectively. Although the characteristic peaks of cubic nickel are still present in CNTs-NH₃, their intensities are obviously reduced, which means that heat treatment with ammonia can eliminate Ni remnants to some extent. As shown in Fig. 2, except for the diffraction peaks of graphitic carbon and nickel residue, there is no obvious difference in the XRD patterns of the supports and the corresponding NiB alloy catalysts, and no other crystalline peaks are present in the patterns of the samples of NiB supported on nanotubes, indicating that the NiB catalysts have an amorphous structure.¹⁷

ICP, BET and TEM measurements

The designed loading of nickel was 25 wt%. The results of ICP measurement show that the actual nickel loading was approximately 16.0 wt% for the two cata-

lysts, *i.e.*, less than the expected loading. This reveals that the surface of the nanotubes was, to some extent, hydrophobic even though carboxylic, hydroxyl or nitrogen-containing basic groups had been introduced during the pretreatment of the nanotubes with nitric acid or ammonia. From the results of BET, the specific surface area increased from 84.2 m²/g for the raw material to 101.3 m²/g for CNTs-HNO₃ and to 99.8 m²/g for CNTs-NH₃ (Table I). The increase in the surface areas of the treated CNTs indicates that refluxing in nitric acid or heat treatment in ammonia had opened the ends of the CNTs. After the supporting of nickel boride, the surface areas of CNTs-HNO₃ and CNTs-NH₃ decreased by 15.9 m²/g and 18.1 m²/g, respectively, which shows that the cavities of nanotubes were partially blocked by the NiB alloy.

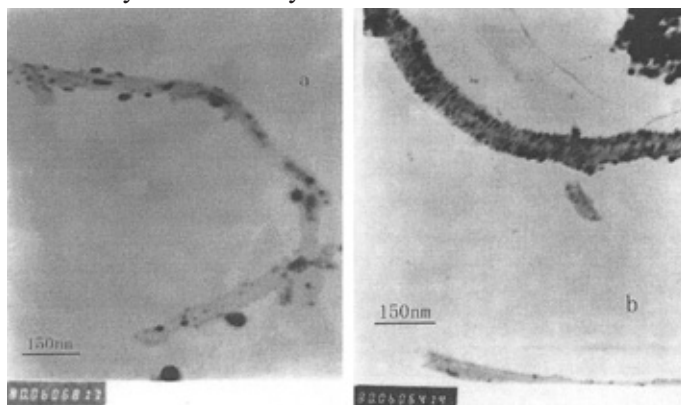


Fig. 3. TEM images of the catalysts (a: NiB/CNTs-HNO₃, b: NiB/CNTs-NH₃).

The TEM microphotographs of NiB/CNTs-HNO₃ and NiB/CNTs-NH₃ amorphous catalysts are shown in Fig. 3. From Fig. 3a it can be seen that the diameters of free NiB particles range from 36 nm to 50 nm, whereas those deposited on the nanotubes are smaller, in the range of 13–23 nm with an average size of about 16 nm. On the other hand, as shown in Fig. 3b, a high density and homogeneous dispersion of NiB particles, with a mean size of 9 nm, were successfully obtained on the CNTs-NH₃ carrier. Clearly, well-dispersed and smaller NiB nanoparticles were formed on the surface of CNTs-NH₃ although it was more difficult to remove the residual Ni effectively by treatment with ammonia than was the case with nitric acid. This demonstrates that the treatment with ammonia plays an important role in the formation of a high density of 9 nm NiB particles homogeneously on CNTs.

Catalytic performance

Typical acetylene-conversion and ethylene-selectivity curves obtained using NiB/CNTs-HNO₃ and NiB/CNTs-NH₃ amorphous catalysts under comparative conditions are shown in Fig. 4. As is apparent, higher values of activity and selectivity were obtained with the latter than with the former catalyst. It is noteworthy that in control experiment, acetylene conversion was not observed on the CNTs-NH₃ carrier without NiB amorphous alloy. ICP measurements showed that the nickel loading on

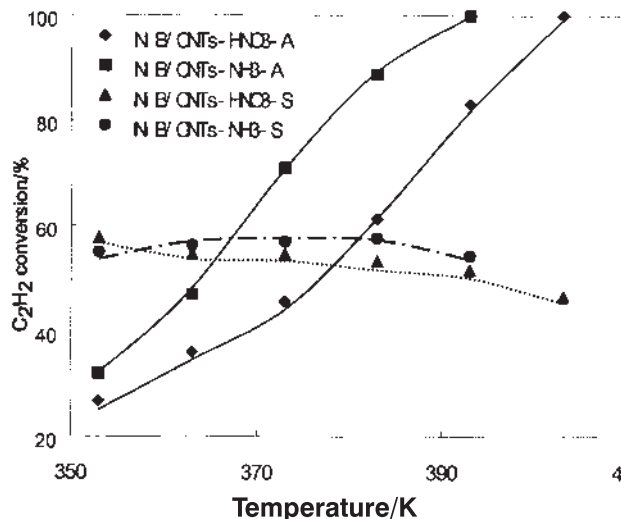


Fig. 4. Influence of the pretreatment of CNTs on acetylene conversion and ethylene selectivity over NiB amorphous catalysts. 410 A: Conversion of C_2H_2 , S: Selectivity of C_2H_4 .

the two catalysts was similar. Thus, the excellent performance of NiB/CNTs-NH₃ arises from its unique structure but not from the residual nickel in the CNTs and the discrepancy of the nickel loading. As reported in the literature, the selective hydrogenation of acetylene often involves complicated reactions occurring simultaneously on the catalyst surface, such as competitive hydrogenation, oligomer and deposit formation.^{18,19} The proposed surface intermediates in the hydrogenation of acetylene are shown in Fig. 5. Multiple bound surface intermediates, such as ethylidyne (4) and ethylidene (5), are hydrogenated to ethane whereas vinylidene (7) is assumed to participate in the formation of oligomers and benzene.^{18,19} These reactions only consume acetylene but do not produce ethylene and thus decrease the selectivity of ethylene. Apparently, the adsorption of ethylidyne, ethylidene and vinylidene species requires multiple sites, namely adjacent two or three Ni atoms.^{20,21} Therefore, the activity and selectivity of the catalysts are closely correlated to the dispersion and morphology of the NiB particles on the surface of the nanotubes. As shown by TEM, well-dispersed and smaller NiB nanoparticles were formed on the surface of CNTs-NH₃, implying a high dispersion of the active nickel component, in other words, a low possibility of the presence of two or three adjacent Ni atoms. Undoubtedly, this would suppress the production of ethane, oligomers and benzene. It is obvious that small NiB nanoparticles dispersed homogeneously along the nanotubes would accelerate the hydrogenation rate and increase the selectivity of ethylene.

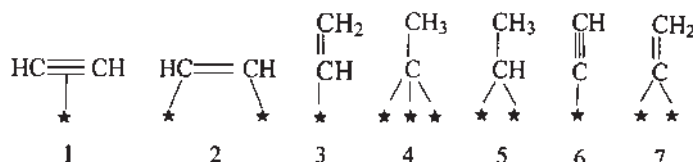


Fig. 5. Proposed surface intermediates in the hydrogenation of acetylene.¹⁹

CONCLUSION

In summary, comparison of the pretreatment of CNTs in nitric acid with that in ammonia showed that carboxylic and hydroxyl functional groups were introduced on the nanotubes during the acid process but basic groups containing nitrogen, such as N–H and C–N, were introduced on the nanotubes during the ammonia process. The nickel catalyst was effectively removed from the CNTs by the acid treatment. TEM measurements showed that a high density of about 9 nm sized NiB particles were dispersed homogeneously on the CNTs-NH₃. However, NiB particles (13–23 nm) with a mean size of 16 nm were scattered on the CNTs-HNO₃. As a result, the activity and selectivity of NiB/CNTs-NH₃ were higher than those of NiB/CNTs-HNO₃ in the selective hydrogenation of acetylene.

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ИЗВОД

ИСПИТИВАЊЕ ПРЕТРЕТМАНА УГЉЕНИЧНИХ НАНОТУБА (CNT) И УТИЦАЈА НА ОСОБИНЕ АМОРФНОГ КАТАЛИЗАТОРА NiB/CNT

CHANG YUAN HU, FENG YI LI, LI HUA и RONG BIN ZHANG

¹Department of Chemistry, Nanchang University, Nanchang, Jiangxi 330047, P. R. and ²Jiangxi Key Laboratory of Nationals Surface Engineering, Jiangxi Science and Technology Normal University, P.O. Box 224, Nanchang 330013, P.R. China

Синтетисане угљеничне нанотубе су третиране азотном киселином (CNTs-HNO₃) или амонијаком (CNTs-NH₃). Фуријеова инфрацрвена спектроскопија (FTIR) је показала да карбоксилне и хидроксилене функционалне групе утичу на функционализацију површине нанотуба после киселинског третмана док се након третмана базом на површини јављају групе које садрже азот, као што су N–H и C–N. Рендгенска дифракција указује да се киселинским третманом отклањају остаци никла из CNT. Међутим, остаци никла су само делимично отклоњени у случају предтретмана са амонијаком. NiB аморфни катализатори нанети на CNTs-HNO₃ и CNTs-NH₃ припремљени редукционом импрегнационом методом су окарактерисани трансмисионом електронском микроскопијом (ТЕМ) као и индуковано куплованом плазмом (ICP), а затим је испитана селективна хидрогенизација ацетилена. ТЕМ мерења су показала велику густину NiB чије су честице од 9 nm хомогено дисперговане на CNTs-NH₃. Међутим, на CNTs-HNO₃ су запажене честице NiB (13–23 nm) средње величине 16 nm. Као последица тога, активност и селективност у хидрогенизацији ацетилена на NiB/CNTs-NH₃ су знатно веће него код катализатора NiB/CNTs-HNO₃.

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