CeO₂助 Ni/MgO 催化剂用于化学气相沉积法制备多壁碳纳米管

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摘要: 以柠檬酸燃烧法制备的 Ni/MgO, Ni/CeO₂-MgO 和 Ni/CeO₂ 为催化剂, CH₄ 为碳源, 采用化学气相沉积法制备多壁碳纳米管 (MWCNTs), 通过 N₂ 吸附、X 射线衍射、H₂ 程序升温还原和 X 射线光电子能谱对催化剂进行表征, 并运用热重和透射电镜表征了碳纳米管的质量和形貌。结果表明, CeO₂ 的加入可有效地降低还原温度和增加易还原 Ni 物种的含量, 并使电子发生转移, 还原后的 Ni/CeO₂-MgO 催化剂中, Ni 晶粒尺寸较小。这表明 CeO₂ 的加入使得 Ni 物种的化学环境发生改变, 导致它和载体间的相互作用减弱, 从而促进 Ni 物种的还原, 且还原后, 高度分散在 CeO₂-MgO 载体上, 从而催化剂的催化活性增加。相比 Ni/MgO 催化剂, Ni/CeO₂-MgO 为催化剂上生长的 CNTs 质量更高。另外, 由 CeO₂ 助 Ni/MgO 催化剂制备出基本没有无定形碳、结晶度好的碳纳米管。

关键词: 镍; 氧化镁; 二氧化铈; 化学气相沉积法; 碳纳米管; 甲烷裂解

中图分类号: O643

文献标识码: A

收稿日期: 2011-03-28. 接受日期: 2011-04-25.

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基金来源: 中央高校基本科研业务费 (2010SCU22010); 国家重点基础研究发展计划 (973 计划, 2011CB201202).

本文的英文电子版(国际版)由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18722067>).

Cerium Oxide Promoted Ni/MgO Catalyst for the Synthesis of Multi-walled Carbon Nanotubes

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Abstract: Ni/MgO, Ni/CeO₂-MgO, and Ni/CeO₂ catalysts were prepared by the citric acid combustion method. Their catalytic properties for the synthesis of multi-walled carbon nanotubes (MWCNTs) by chemical vapor deposition using CH₄ as carbon source were evaluated. The catalysts were characterized with N₂ adsorption, X-ray diffraction (XRD), H₂ temperature-programmed reduction (H₂-TPR), and X-ray photoelectron spectroscopy (XPS). The quality and structure of the CNTs were characterized by thermogravimetry (TG) and transmission electron microscopy (TEM). H₂-TPR showed that CeO₂ helped decrease the reduction temperature and increase the content of an easily reducible Ni species. XPS showed an energy shift of the Ni catalyst that was modified by CeO₂. XRD showed that the reduced nickel maintained their small particle sizes in the Ni/CeO₂-MgO catalysts. These findings suggested that the addition of CeO₂ changed the chemical environment of the nickel species, which resulted in a weaker interaction between the nickel and the support and increased the reducibility of the Ni species. Moreover, the reduced nickel was highly dispersed on the CeO₂-MgO support. The change enhanced the catalytic activity for the growth of carbon nanotubes (CNTs). Characterization by TG and TEM showed that the quality of the CNTs grown on Ni/CeO₂-MgO was better than those grown on Ni/MgO catalyst.

Key words: nickel; magnesium oxide; cerium oxide; chemical vapor deposition method; carbon nanotubes; methane decomposition

Received 28 March 2011. Accepted 25 April 2011.

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This work was supported by the Fundamental Research Funds for the Central Universities (2010SCU22010) and the National Basic Research Program of China (973 Program, 2011CB201202).

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

Carbon nanotubes (CNTs) have attracted significant research interest since their discovery by Iijima in 1991 [1]. CNTs have remarkable properties that make them suitable for a wide range of applications as chemical sensors [2], composite materials [3], electronic devices and so on. There are three techniques commonly used to grow CNTs, namely, arc discharge, laser ablation, and chemical vapor deposition (CVD). Among these, CVD is the most convenient way to grow all kinds of CNTs and the best choice to produce large amount of CNTs at relatively low cost and with mild growth conditions.

The carbon sources used include CH_4 [4], C_2H_4 , C_2H_2 [5], CO [6], ethanol [7] and so on, and is also one of main factors influencing the quality of the CNTs. Among the hydrocarbons, methane as the carbon source produce less impurity in the synthesized CNTs because it is difficult to decompose it in the gas phase and on the support.

In the CVD synthesis of CNTs, Fe, Co, Ni, and their alloys [8] supported on oxides such as Al_2O_3 , SiO_2 , and MgO [9] are used as the catalyst. MgO is considered a good support for the catalyst from the viewpoint of convenience and cost to purify the CNT product since MgO can be easily dissolved in dilute HCl solution.

A rare earth component Ce in a Ni or Fe catalyst played an important role in the synthesis of single-walled carbon nanotubes using arc discharge [10,11] and the CVD method [12]. The addition of Ce prevented the sintering of Ni particles during reduction and maintained its distribution, which promoted the stability of the Ni catalyst [13]. Gueara et al. [14] found that Ni on a high surface area Ce-MCM-41 support showed excellent activity for methane decomposition.

In this work, $\text{Ni/CeO}_2\text{-MgO}$ catalysts were prepared using the citric acid combustion method and used to synthesize CNTs by the CVD method using methane as the carbon source. The catalysts and CNTs were characterized by H_2 temperature-programmed reduction ($\text{H}_2\text{-TPR}$), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and thermogravimetry (TG). The results showed that the $\text{Ni/CeO}_2\text{-MgO}$ catalyst had good catalytic activity for the decomposition of methane to synthesize CNTs.

1 Experimental

1.1 Preparation of the catalysts

The catalyst precursors for $\text{Ni/CeO}_2\text{-MgO}$ were prepared by the citric acid combustion method. $\text{Ni}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, and $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ were mixed in a citric acid aqueous solution that was stirred and gelated at $70\text{ }^\circ\text{C}$. After drying at $120\text{ }^\circ\text{C}$ overnight, the dried gel was calcined at $600\text{ }^\circ\text{C}$ for 2 h in air to get the $\text{Ni/CeO}_2\text{-MgO}$ catalyst.

The loading of Ni on the catalysts was kept at 50 wt%. The contents of CeO_2 were 0%, 20%, 40%, and 50% for four different catalysts, and the remaining component was MgO . For example, the $\text{Ni/20CeO}_2\text{-MgO}$ catalyst had the weight ratio of $\text{Ni:CeO}_2\text{:MgO}$ of 50:20:30. For comparison, Ni/MgO and Ni/CeO_2 were also prepared by the same method.

1.2 Characterization of catalyst and carbon nanotubes

The specific surface areas of the catalysts were determined by N_2 adsorption at $-196\text{ }^\circ\text{C}$ on a Quantachrome Nova 1000e apparatus. $\text{H}_2\text{-TPR}$ measurements were carried out at atmospheric pressure with a fixed bed reactor. The sample (50 mg) was loaded and the reduction gas of 5% H_2 -95% N_2 was introduced at a flow rate of 30 ml/min. The temperature of the reactor was increased linearly at a rate of $5\text{ }^\circ\text{C/min}$ from 50 to $850\text{ }^\circ\text{C}$ and kept for 30 min at $850\text{ }^\circ\text{C}$. The effluent stream was analyzed for hydrogen by a thermal conductivity detector. Phase analysis was performed by XRD using a D/MAX-2500 (Rigaku Company) diffractometer with Cu K_α ($\lambda = 0.154056\text{ nm}$) radiation. Data for the Bragg angle from 10° to 90° were collected. XPS experiments were performed on an XSAM800 spectrometer with an Al anode for K_α ($h\nu = 1486.6\text{ eV}$) radiation. Charging effects were corrected by adjusting the binding energies using the C 1s peak from carbon contamination at 284.6 eV . TG experiments were carried out under flowing air with a heating rate of $15\text{ }^\circ\text{C/min}$. TEM images were taken with a Tecnai G2 F20 S-Twin microscope at an accelerating voltage of 200 kV.

1.3 Synthesis of carbon nanotubes

To grow CNTs, 0.03 g of catalyst powder was dispersed on each of three boats that were then placed in a horizontal quartz reactor (inner diameter = 3 cm). First, the catalyst powder was reduced in situ in H_2 at $550\text{ }^\circ\text{C}$ for 1 h. Subsequently, the sample was heated to $650\text{ }^\circ\text{C}$ in flowing N_2 and then the flow was switched to high purity methane (100 ml/min) for the cracking reaction of methane. After one hour's reaction, the CNTs grown were cooled to room temperature in a N_2 atmosphere.

2 Results and discussion

2.1 N_2 adsorption results

Table 1 presents the data for the specific surface areas of the catalysts. The specific surface areas of the catalysts in decreasing order were: $\text{Ni/MgO} > \text{Ni/20CeO}_2\text{-MgO} > \text{Ni/40CeO}_2\text{-MgO} > \text{Ni/50CeO}_2$. The specific surface areas

of the catalysts decreased with the increasing CeO₂ content in them. Compared with the other catalysts, the specific surface area of Ni/50CeO₂ catalyst was decreased significantly due to the absence of Mg. This would result in a low catalytic activity for the synthesis of CNTs using Ni/50CeO₂ as the catalyst.

Table 1 Specific surface areas of the different catalysts

Catalyst	Ni/MgO	Ni/20CeO ₂ -MgO	Ni/40CeO ₂ -MgO	Ni/50CeO ₂
$A_{\text{BET}}/(\text{m}^2/\text{g})$	106.3	77.99	62.59	26.28

2.2 H₂-TPR characterization and analysis

The redox properties of the catalysts were investigated with H₂-TPR experiments. The profiles are shown in Fig. 1. The H₂-TPR profile of Ni/MgO showed a broad reduction band. The main reduction peak appearing at 770 °C was assigned to the reduction of Ni species interacting strongly with the support and the weak reduction peak at 500 °C was attributed to the reduction of Ni species which had a weak interaction with the support. Arena et al. [15] reported that the most reactive forms of NiO had undergone a progressive diffusion into the MgO lattice, and likely formed a NiO·MgO solid solution when the reduction temperature was higher than 600 °C. So, most the nickel species were in the form of a solid solution in the Ni/MgO catalyst, as the reduction temperature of these nickel species was higher than 600 °C.

For catalysts with the composite support, the main reduction peak of the nickel species appeared at 525 °C for Ni/20CeO₂-MgO and at 460 °C for Ni/40CeO₂-MgO. The reduction temperature of nickel decreased with increasing CeO₂ content. There were two main reasons for the decrease of reduction temperature. First, the addition of CeO₂ inhibited the forming of a NiO·MgO solid solution. When the reduction temperature was higher than 600 °C, hydrogen consumption by the Ni/CeO₂-MgO catalysts decreased sig-

Fig. 1. H₂-TPR profiles of the catalysts. (1) Ni/MgO; (2) Ni/20CeO₂-MgO; (3) Ni/40CeO₂-MgO; (4) Ni/50CeO₂; (5) CeO₂.

nificantly relative to the Ni/MgO catalyst. Second, a spillover effect of hydrogen on CeO₂ also led to a decrease of the deoxidization temperature. The spillover effect of CeO₂ can be explained by that H₂ molecules adsorbed on the surface of CeO₂ spillover onto the NiO phase, which promoted the reduction of NiO [16]. At the same time, the reduction of nickel was easy to sinter for the Ni/50CeO₂ catalyst, as much nickel species was reduced at a low temperature (380 °C). This was proved by XRD result as follows. The decrease of reduction temperature and promotion of reduction degree of the nickel species provided more active sites for the growth of CNTs. A weak reduction peak appearing at 850 °C in the H₂-TPR of CeO₂ can be attributed to the reduction of Ce⁴⁺ to Ce³⁺. Similar reduction peaks were observed for the other catalyst samples.

2.3 XPS characterization and analysis

To further study the effects of cerium in these Ni-based catalysts, the Ni/MgO, Ni/20CeO₂-MgO, Ni/40CeO₂-MgO, and Ni/50CeO₂ samples were characterized by XPS. The Ni 2p_{3/2} spectra and the corresponding Ni 2p_{3/2} binding energy values of these samples are shown in Fig. 2. A typical Ni 2p_{3/2} XPS spectrum of the Ni/MgO sample showed peaks at 855.01 and 861.22 eV. The peak at 861.22 eV was ascribed to a satellite peak of 855.01 eV. This catalyst had a higher Ni 2p_{3/2} binding energy relative to NiO (854.5 eV) [17], which indicated that electron transfer took place from Ni to Mg. When Ce was added into the Ni/MgO sample, the Ni 2p_{3/2} peak binding energy shifted from 855.01 to 854.73 and 854.67 eV for Ni/20CeO₂-MgO and Ni/40CeO₂-MgO, re-

Fig. 2. Ni 2p_{3/2} XPS spectra of various samples. (1) Ni/MgO; (2) Ni/20CeO₂-MgO; (3) Ni/40CeO₂-MgO; (4) Ni/50CeO₂.

spectively. The significant differences in the Ni $2p_{3/2}$ energies between the Ni/MgO and Ni/CeO₂-MgO samples suggested that the chemical environment or structure surrounding the Ni ions were changed by the Ce element. The strong electron-withdrawing property of Mg made interaction strong between Ni species and support resulting in difficult reduction Ni species for the Ni/MgO catalyst [18]. The Ni in Ni/CeO₂-MgO was electron-rich compared with the Ni in the Ni/MgO sample. This result implied that the interaction between the nickel species and support was weakened in cerium oxide promoted Ni/MgO.

2.4 XRD characterization and analysis

Figure 3 shows the powder XRD patterns of the Ni/MgO, Ni/CeO₂-MgO, and Ni/CeO₂ catalysts. These patterns have the same prominent reflections that can be assigned to NiO, a solid solution NiO·MgO and MgO or a mixture of the three phases in unknown concentrations [19]. It is well known that the crystal type of MgO and NiO is cubic NaCl. Moreover, Ni²⁺ (0.07 nm) and Mg²⁺ (0.065 nm) have similar ionic radii [18]. Therefore, oxide solid solutions of NiO·MgO can be formed with any ratio of MgO to NiO without significant structural changes that can be detected by XRD. After addition the CeO₂ into Ni/MgO, the only remarkable feature observed in the powder XRD patterns was a progressive broadening of the respective reflection and diffraction peak of CeO₂, which became progressively narrower. This indicated CeO₂ inhibited crystal formation in Ni/MgO. In the Ni/50CeO₂ catalyst, the diffraction peak of NiO became narrower than for the MgO free sample.

To understand the nature of the nickel formed after the reduction of the catalysts, Ni/20CeO₂-MgO, Ni/40CeO₂-MgO, and Ni/50CeO₂ were reduced at 550 °C. Subse-

Fig. 3. Powder XRD patterns of the fresh catalysts. (1) Ni/MgO; (2) Ni/20CeO₂-MgO; (3) Ni/40CeO₂-MgO; (4) Ni/50CeO₂.

quently, XRD data (Fig. 3) were collected from the reduced catalysts. Figure 4 shows the XRD patterns of these samples. The XRD data showed peaks due to the nickel, MgO, and CeO₂ phases. The three intense XRD peaks of $2\theta = 44.5^\circ$, 51.8° , and 76.5° corresponded to the diffraction peaks of Ni. The intensities of the nickel peaks were not evidently different for Ni/20CeO₂-MgO and Ni/40CeO₂-MgO, but the diffraction peak of nickel became sharp with Ni/50CeO₂. The particle sizes of nickel were 9.2, 8.9, and 13.2 nm for Ni/20CeO₂-MgO, Ni/40CeO₂, and Ni/50CeO₂, respectively, which were estimated from the X-ray line broadening of the nickel peak at 51.8° . From the XRD results, the particle sizes of reduced nickel were maintained at around 9 nm. There was no sintering of the Ni/CeO₂-MgO catalysts, which implied reduced nickel was highly dispersed on the support. However reduced nickel was sintered in Ni/50CeO₂, resulting in the forming of large particles of Ni due to the high reducibility and the low reduction temperature of the active phase shown by the H₂-TPR results.

Fig. 4. Powder XRD patterns of the catalysts after reduction at 550 °C for 1 h. (1) Ni/20CeO₂-MgO; (2) Ni/40CeO₂-MgO; (3) Ni/50CeO₂.

2.5 Catalytic properties for the growth of carbon nanotubes

Figure 5 illustrates the yield of carbon nanotubes from the different catalysts. The addition of CeO₂ significantly affected the catalytic activities of the Ni/MgO catalysts. The CNT yields from Ni/MgO, Ni/20CeO₂-MgO, Ni/40CeO₂-MgO, and Ni/50CeO₂ were 0.41, 3.61, 7.53, and 1.77 g/g, respectively. The result showed that the addition CeO₂ into the Ni/MgO catalyst gave a high catalytic activity for the growth of CNTs. It should be noted that the catalytic activity of Ni/50CeO₂ was significantly lower due to the low surface area and formation of large particles of nickel in the reduction process, which were shown by the BET and XRD analysis.

Fig. 5. Yield of CNTs with different catalysts at the synthesis temperature of 650 °C for 1 h.

2.6 TEM characterization and analysis

The structure and morphology of the CNTs were observed using TEM images. Figure 6 shows the microstructure of the CNTs obtained from the Ni/MgO and Ni/40CeO₂-MgO catalysts. As shown in Fig. 6(a), a lot of bead-like carbon deposits and twisted CNTs were formed, while the black catalyst particles were encapsulated by graphitic carbon that greatly inhibited the contact of catalyst and CH₄. This also provided more evidence to explain the low activity of the Ni/MgO catalyst. Figure 6(b) showed TEM images of the CNTs grown on the Ni/40CeO₂-MgO catalyst. A very high density of carbon nanotubes was observed. These possessed a well-crystallized multi-walled carbon nanotubes (MWCNTs) structure with almost no amorphous carbon and catalyst particles on their surface. Some CNTs of large diameters can be found in Fig. 6(b). The diameter of the carbon nanotubes greatly depends on the size of metal particles: larger Ni particles lead to CNTs with larger diameters. Some nanoparticles that had agglomerated in the reduction process would be responsible for this. Cui et al. [20] found that the growth of CNTs had lengthening and thickening stages. The CNTs were thickened substantially and the catalysts deactivated in the thickening stage. In the lengthening stage, the catalysts preserved their activity. The CNTs grown on the Ni/20CeO₂-MgO catalyst were longer and thinner than those

Fig. 6. TEM images of CNTs grown on Ni/MgO (a) and Ni/40CeO₂-MgO (b).

grown on the Ni/MgO catalyst. This implied the composite supports catalyst gave better catalytic activity. TEM analysis also showed that spherical catalyst particles became elongated after the synthesis of CNTs (circled in Fig. 6(a)). This elongation of the nanoparticles may be due to the strong interaction between the CNTs and the catalyst. Similar changes to the particles were found by Rummeli et al. [21].

2.7 TG characterization and analysis

Thermogravimetry analysis is an important analytical technique to show the quality of CNTs. It is used to quantitatively measure thermal stability, purity, and homogeneity [22]. Thermal stability is dependent upon a number of factors, e.g., defect density [23]. Three weight losses are recorded when the samples were heated in air. Those losses were attributed to the removal of amorphous carbon (300–350 °C), CNTs (400–650 °C) [23], and massive graphite carbon (> 700 °C) [24] at the different temperatures. Figure 7 illustrated the TG and DTG curves of the CNTs grown on the Ni/MgO and Ni/40CeO₂-MgO catalysts. The TG results showed that the main weight losses were in the range of 380–600 and 470–680 °C for the CNTs grown on the Ni/MgO and Ni/40CeO₂-MgO catalysts, respectively. As shown in Fig. 7(a), the weight loss was about 3 wt% before 350 °C from the sample grown on Ni/MgO, which indicated some impurity carbon existed. Moreover, Fig. 7 showed that the weight loss curve of the CNTs grown on Ni/40CeO₂-MgO shifted to a higher temperature (from 509.9 to 626.8 °C) as compared with those grown on the Ni/MgO catalyst, and a narrower temperature range was observed. The weight loss of the CNTs grown on the Ni/MgO catalyst was lower because the Ni/MgO catalyst

Fig. 7. TG and DTG curves of the as-prepared materials. (a) Ni/MgO; (b) Ni/40CeO₂-MgO.

deactivated easily, which increased the residual catalyst content [23]. The presence of numerous defects along the twisted walls also probably lowered the relative thermal stability of the CNTs on Ni/MgO as these defects promoted oxidative combustion by providing edges and dangling bonds [8]. The oxidation temperature of the CNTs grown on the Ni/40CeO₂-MgO catalyst was associated with pure, less defective, and highly crystallized CNTs. The TG results further indicated that pure and well-crystallized CNTs were grown on the Ni/40CeO₂-MgO catalyst.

3 Conclusions

The addition of CeO₂ to a Ni/MgO catalyst caused more facile reducibility of the Ni species because the formation of a hardly reducible solid solution was inhibited. The reduced nickel retained a small nanoparticle size. XPS demonstrated that the Ce species affected the chemical environment of the Ni species. As a result, the Ni/CeO₂-MgO catalysts exhibited higher activities for the growth of CNTs. TEM and TG analyses showed that the Ni/MgO catalyst was much covered by graphitic carbon that inhibited interaction with the carbon source gas and consequently gave a lower activity for carbon nanotube growth. In contrast, the CNT yield obtained from the Ni/40CeO₂-MgO catalyst was promoted and the CNTs obtained were pure with a well-crystallized structure.

Acknowledgements

The authors would like to thank Dr. Liu Ming and the TEM Group of Analytical Testing Center of Sichuan University.

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