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Article

Comparison of growth mechanisms of undoped and nitrogen-doped carbon nanofibers on nickel-containing catalysts

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ARTICLE INFO

Article history:

Received 28 August 2015

Accepted 30 September 2015

Published 5 January 2016

Keywords:

Carbon nanofibers

Nitrogen doping

Growth mechanism

Nickel-based catalyst

ABSTRACT

The growth mechanisms of carbon nanofibers on Ni catalysts and nitrogen-doped carbon nanofibers on Ni and Ni-Cu catalysts were studied. The growth of both types of nanofibers was found to occur by a mechanism that included the formation of surface non-stoichiometric nickel carbide followed by the dissolution and diffusion of carbon, or carbon and nitrogen into the bulk of the catalyst particles.

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1. Introduction

The synthesis of carbon nanomaterials (CNMs) is a rapidly growing area of nanotechnology [1–5]. CNMs possess various useful properties, which extend the scope of the applications of such materials in different fields [1,2,4,6–9]. To ensure efficient control of CNM syntheses, the precise detail of their formation processes should be elucidated. The mechanism underlying the formation of undoped CNMs from hydrocarbons on metal catalysts has been discussed in many works [10–12]. It has been concluded that the formation of CNMs on metal catalysts proceeds by the following steps: (1) catalytic decomposition of a hydrocarbon on the surface of a metal particle to form atomic carbon, and an increase in carbon concentration to limiting values; (2) dissolution of carbon atoms and diffusion through the bulk of the metal particle; (3) formation of graphite phase nucleation centers and growth of the phase to produce carbon

nanotubes or carbon nanofibers (CNFs).

This proposed mechanism suggests that the diffusion of carbon atoms is caused by concentration gradients at the particle surfaces, where hydrocarbons are decomposed and where CNMs are formed. However, irrespective of the substantial progress that has been made in understanding the mechanism of CNM formation, some aspects remain debatable, for example, the type of carbon diffusion (bulk, surface, or subsurface) [13].

The synthesis of nitrogen-doped carbon nanomaterials (N-CNMs) is a new field that is currently receiving much attention [14–19]. Methods and approaches used to produce N-CNMs are based either on the direct formation of material from a nitrogen-containing carbon precursor or on the heat treatment of undoped CNMs in a nitrogen-containing medium. Thus, the synthesis method can be catalytic (low-temperature) or physical (high-temperature). The catalytic synthesis of N-CNMs on the iron subgroup metals (Fe, Co, Ni) is a direct

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method, which proceeds at moderate temperatures and results in selective formation of the target product. This has advantages compared with physical methods such as laser ablation, electric arc synthesis, or magnetron sputtering. The main emphasis in the development of methods for N-CNM synthesis and the investigation of their properties has been placed on carbon nanotubes doped with nitrogen. In contrast to such nanotubes, the multiple edges of graphite planes in CNFs come to the outer surface of the fiber, thus increasing the interaction of the surface with active components and making CNFs especially attractive for catalytic applications [1,4,5,20–25].

It should be noted that there is currently a very limited understanding of the mechanism of the catalytic growth of N-CNMs, in particular N-CNFs, on metal catalysts (Fe, Co, Ni). It is commonly accepted that the growth mechanism of N-CNMs is similar to that of undoped CNMs. The only difference is that the decomposition of the nitrogen-containing compound is accompanied by the additional formation of atomic nitrogen, which also diffuses over the surface of the catalyst particle or through its bulk [26–28]. However, there are limited experimental data in favor of this hypothesis [29–32]. As shown in our earlier works, the conditions of N-CNF formation by decomposition of ethylene-ammonia mixture on a Ni-Cu catalyst, in particular the temperature and ammonia concentration, determine the state of the catalyst during its growth and, as a result, the properties of the resulting N-CNFs [30,32]. The present work aimed to reveal and compare the mechanisms of CNF and N-CNF growth on Ni and Ni-Cu catalysts.

2. Experimental

In this study, a Ni catalyst was synthesized using the reactive “pure” Ni(II) oxide. Metallic nickel was obtained by the reduction of NiO in hydrogen at 300 °C. Reduction, carbide formation, and carbonization of the catalyst were carried out in a flow-type reactor equipped with a quartz balance. This setup made it possible to directly monitor changes in the sample mass during the experiment. Details of the setup design can be found elsewhere [33]. The mass measurement sensitivity was 1×10^{-4} g. The initial catalyst loading was varied within the range 0.002–0.100 g. At the beginning of the experiment, the sample was heated under an argon flow to the chosen working temperature. The argon supply was then shut off and the reaction mixture was fed into the reactor.

The formation kinetics of nickel carbide were studied at 225–300 °C, while those of CNFs on nickel were studied at 500–650 °C in an argon-diluted 1,3-butadiene medium. To prevent sintering of the reduced metallic nickel, the studies at 500–650 °C were conducted with the sample containing 20 wt.% carbon. This sample was synthesized by treating NiO with argon-diluted 1,3-butadiene ($P(\text{C}_4\text{H}_6) = 10.5$ kPa, $T = 600$ °C).

Changes in the phase composition of the nickel catalyst upon decomposition of 1,3-butadiene were investigated using a high-temperature chamber mounted on a standard laboratory diffractometer (DRON-1) with a copper anode and graphite monochromator, as shown in Fig. 1.

X-ray diffraction (XRD) measurements of the decomposition

Fig. 1. High-temperature X-ray chamber for study of nickel catalyst during decomposition of 1,3-butadiene.

of ethylene and ethylene-ammonia mixtures were performed using synchrotron radiation at the Siberian Synchrotron and Terahertz Radiation Center (Novosibirsk, Russia) on a diffractometer with a position-sensitive detector and operating wavelength $\lambda = 0.1731$ nm.

The XRD study was carried out with a catalyst composed of 65 wt.% Ni/25 wt.% Cu/10 wt.% Al₂O₃ (Ni-Cu), which has previously been shown to possess high catalytic activity and stability for the formation of N-CNFs by decomposition of ethylene-ammonia mixture [34]. For comparison, a catalyst composed of 90 wt.% Ni/10 wt.% Al₂O₃ (Ni) was also used in the experiments. Both catalysts were synthesized by co-precipitation from an aqueous solution of the required nitrates with an aqueous solution of NaOH. The dried samples were calcined in nitrogen at 350 °C and then reduced in flowing hydrogen at 550 °C.

Time-resolved XRD was used for *in situ* study of the catalysts during N-CNF growth by decomposition of 100% C₂H₄ as well as 75% C₂H₄/25%NH₃ and 50% C₂H₄/50% NH₃ mixtures. For this experiment, the diffractometer was equipped with a high-temperature reactor chamber (XRK-900, Anton Paar, Austria). The test sample was loaded into an open holder and mounted in the reactor chamber. The reactor chamber design allowed the reaction mixture to pass through the bulk of the sample. The catalyst was pretreated in hydrogen medium at 550 °C for 15 min to remove adsorbed oxygen from the catalyst surface. The reaction mixture was then fed into the reactor chamber at a rate of 40 mL/min. The sample was held at 550 °C in the reaction mixture flow and XRD patterns were recorded at 30 s intervals.

The amount of nitrogen in the N-CNFs was determined by elemental analysis. The charge states of nitrogen in the N-CNFs and nickel in the CNFs and N-CNFs were analyzed by X-ray photoelectron spectroscopy (XPS). After the reaction, the samples were quenched in argon medium to prevent further changes in the catalysts. Spectra were collected on a KRATOS

ES300 photoelectron spectrometer with non-monochromatized Al K_{α} radiation (photon energy of 1486.6 eV). The core-level Au 4f_{7/2} gold line with the binding energy of 84.0 eV was used for spectrometer calibration. Survey spectra were acquired at an analyzer transmission energy of 50 eV and steps of 1.0 eV. The narrow spectral regions were measured at an analyzer transmission energy of 25 eV and steps of 0.1 eV.

TEM images were obtained on a JEM-2010 (JEOL) instrument at a 200-kV accelerating voltage and 0.14 nm resolution. Samples for TEM imaging were supported on a holey carbon film fixed on copper or molybdenum grids using an ultrasonic dispenser.

3. Results and discussion

3.1. Decomposition of 1,3-butadiene on Ni catalyst

XRD studies performed with a standard DRON-1 laboratory diffractometer and a high-temperature X-ray chamber showed that the decomposition of 1,3-butadiene on Ni at 350 °C led to the formation of a metastable nickel carbide phase (Fig. 2(2)). No changes in the spectrum were observed during exposure of the sample to the 1,3-butadiene medium for 30 min. Thermal treatment of the nickel carbide in helium at 380 °C resulted in its decomposition into metallic nickel and carbon (Fig. 2(3)).

Taking these results into account, the kinetics of nickel carbide formation were studied using a temperature range of 225–300 °C, as shown in Fig. 3. The calculated activation energy of the carbide formation, E_a , was 23 kcal/mol.

Figure 4 illustrates the effect of 1,3-butadiene partial pressure on the rate of nickel carbide formation at 300 °C. The reaction order of Ni₃C formation with respect to 1,3-butadiene was equal to 1. This was determined in the initial period of the reaction (before precipitation of 0.7–0.8 wt.% carbon), i.e., when the formation of carbide and precipitation of CNFs on the nickel surface could not distort the reaction rate. Further growth of the nickel carbide and CNFs inhibited the carbide formation reaction.

At the next stage of the study, we determined the activation energy and reaction order with respect to 1,3-butadiene for the

Fig. 2. Effect of reaction medium and temperature on the phase composition of Ni catalyst. (1) Ni, He:H₂ = 10:1 medium, $T = 350$ °C; (2) Ni + Ni₃C, C₄H₆:He = 1:10 medium, $T = 350$ °C; (3) Ni, He medium, $T = 380$ °C.

Fig. 3. Effect of temperature on the rate of nickel carbide formation at a 1,3-butadiene partial pressure of 0.7 kPa.

formation of CNFs on Ni catalyst at a temperature of 500–650 °C and butadiene partial pressures of 10.5, 3.5, and 1.05 kPa. CNF formation on metallic nickel was found to have a zero reaction order, and activation energy, E_a , of 38 kcal/mol (Fig. 5).

The following conclusions can be derived from the experimental data displayed in Fig. 2. At temperatures up to 350 °C, the interaction of 1,3-butadiene with nickel leads to the formation of metastable Ni₃C phase. The experimental detection of this phase by XRD can be explained by its low rate of decomposition under the chosen conditions. In turn, carbon diffusion through the nickel phase at 500–650 °C became the limiting step in the formation of the CNFs. This assumption is based on the experimentally observed zero order of the CNF formation reaction with respect to hydrocarbon concentration and the fact that the activation energy of carbon diffusion in nickel over the temperature range studied was 33–38 kcal/mol [35], which is close to the activation energy of coking.

3.2. Decomposition of 100% C₂H₄ and C₂H₄/NH₃ mixtures on Ni-Cu catalyst

The phase composition of the initial Ni-Cu catalyst may be

Fig. 4. Effect of 1,3-butadiene partial pressure on the nickel carbide formation at 300 °C.

Fig. 5. Effect of reaction temperature on the rate of CNF formation on nickel at a 1,3-butadiene partial pressure of 10.5 kPa.

represented as a mixture of the nickel-enriched alloy $\text{Ni}_{0.85}\text{Cu}_{0.15}$ ($a = 0.3539 \pm 0.0003$ nm) and the copper-enriched alloy $\text{Cu}_{0.95}\text{Ni}_{0.05}$ ($a = 0.3612 \pm 0.0003$ nm).

During the decomposition of both the 100% C_2H_4 and the 75% $\text{C}_2\text{H}_4/25\%$ NH_3 or 50% $\text{C}_2\text{H}_4/50\%$ NH_3 mixtures, the reflection corresponding to $\text{Ni}_{0.85}\text{Cu}_{0.15}$ shifted to a smaller angle within the first few minutes of the reaction. This indicates an

Table 1

Maximum values of the lattice parameter of the constituent $\text{Ni}_{0.85}\text{Cu}_{0.15}$ and $\text{Cu}_{0.95}\text{Ni}_{0.05}$ alloys of the Ni-Cu catalyst during decomposition of ethylene and ethylene-ammonia mixtures, and nitrogen content of the resulting N-CNFs.

Reaction mixture	Parameter of $\text{Ni}_{0.85}\text{Cu}_{0.15}$ (nm)	Parameter of $\text{Cu}_{0.95}\text{Ni}_{0.05}$ (nm)	[N] (wt.%)
Initial catalyst	0.3561	0.3642	0
100% C_2H_4	0.3575	0.3642	0
75% $\text{C}_2\text{H}_4/25\%$ NH_3	0.3578	0.3642	0.9
50% $\text{C}_2\text{H}_4/50\%$ NH_3	0.3582	0.3642	2.5

increase in the lattice parameter of this alloy caused by carbon dissolution (Fig. 6). During the first 3–7 min of the reaction, depending on the reaction medium, the lattice parameter increased monotonically and then reached a stationary value. Thus, a correlation was observed between the concentration of ammonia in the reaction mixture, the maximum value of the lattice parameter of the alloy observed during the experiment, and the nitrogen concentration in the resulting N-CNFs (Table 1). The position of the reflection corresponding to $\text{Cu}_{0.95}\text{Ni}_{0.05}$ remained virtually constant during the course of the reaction ($a = 0.3642$ nm). A very slight change in the lattice parameter of the Cu-enriched alloy observed in the reaction may be related to enrichment of the alloy surface with nickel. As the time of experiment was extended, a reflection at $\sim 29^\circ$ (0.3456 nm)

Fig. 6. Fragment XRD patterns of the Ni-Cu catalyst in the region of the C(002), Ni(111), Cu(111), Ni(200), and Cu(200) peaks during decomposition of 100% C_2H_4 (a), 75% $\text{C}_2\text{H}_4/25\%$ NH_3 (b), and 50% $\text{C}_2\text{H}_4/50\%$ NH_3 (c), and changes in the lattice parameter of Ni^* and Cu^* alloys during the course of the reaction (d). Ni^* — $\text{Ni}_{0.85}\text{Cu}_{0.15}$; Cu^* — $\text{Cu}_{0.95}\text{Ni}_{0.05}$.

Fig. 7. Fitted N 1s spectra of N-CNFs synthesized by decomposition of 75% C_2H_4 /25% NH_3 (a) and 50% C_2H_4 /50% NH_3 (b) mixtures on the Ni-Cu catalyst.

assigned to the carbon phase appeared in the XRD patterns.

The incorporation of nitrogen into the structure of the carbon nanofibers is supported by the XPS data, which indicated that the nitrogen in the N-CNFs was in three main states: pyridinic with $E_b \approx 398$ eV, pyrrolic with $E_b \approx 399.7$ eV, and graphitic with $E_b = 401\text{--}402$ eV (Fig. 7) [19,23].

The Ni $2p_{3/2}$ spectrum, shown in Fig. 8, consisted of a main peak at 853.8 eV, which can be attributed to nickel in the surface carbide-like state NiC_x [36], and weak maxima at 855 and 856.7 eV corresponding to oxidized states of nickel [37–39].

3.3. Decomposition of 75% C_2H_4 /25% NH_3 mixture on Ni catalyst

No changes in the position or intensity of nickel reflections were observed in the first minutes of N-CNF formation on the Ni catalyst. At approximately the 8 min into the reaction, the nickel reflection started to decrease in intensity and increase in width toward a larger angle (Fig. 9). As a result, a splitting of the reflections became noticeable, as if the sample had decomposed into two phases with identical structures, one having a decreased unit cell parameter. The most intense reflections corresponded to interplanar spacings equal to 0.2047 and 0.2027 nm. Correction for thermal expansion gives interplanar

Fig. 8. Fitted Ni $2p_{3/2}$ spectra of N-CNFs synthesized by decomposition of 75% C_2H_4 /25% NH_3 mixture on the Ni-Cu catalyst.

spacings of 0.2034 and 0.2014 nm. The interplanar spacing of the first phase corresponds to that of cubic nickel Ni (0.2034 nm), but identification of the second phase is rather difficult. As shown in earlier studies, the formation of oversaturated carbon solution in nickel increases the lattice parameter of the nickel [40]. The same is expected to occur upon diffusion of nitrogen atoms through bulk metallic nickel. However, we observed a decrease in the lattice parameter of the second phase compared with that of metallic nickel. Accordingly, one can suppose that this decrease (to 0.2014 nm) is related to partial incorporation of nitrogen and carbon atoms into the cubic lattice of metallic nickel and formation of a cubic phase with a mixed composition of NiC_xN_y .

Similarly to the Ni-Cu catalyst, XPS revealed the formation of a carbide-like species ($E_b = 853.6$ eV) on the surface of the Ni catalyst after the decomposition of 75% C_2H_4 /25% NH_3 mixture.

It should be noted that the Ni catalyst was much less active and stable than the Ni-Cu catalyst for the synthesis of N-CNFs

Fig. 9. Fragment XRD patterns of the Ni catalyst in the region of Ni(111) and Ni(200) lines during decomposition of 75% C_2H_4 /25% NH_3 mixture.

[34]. The nitrogen content of the N-CNF catalyst after the decomposition of 75% C_2H_4 /25% NH_3 mixture was 0.5 wt.%.

3.4. Comparison of the growth mechanisms of CNFs and N-CNFs on metal catalysts

As has been demonstrated in many works, in particular Ref. [10], the growth of CNFs on the catalysts proceeded by a mechanism that included the formation of a carbide-like intermediate on the front surface of the particle, its decomposition, carbon diffusion through the particle, and CNF growth.

The state of the carbon on the surface and in the bulk metal during the growth of CNMs is still a controversial question. Primarily, it has been assumed that dissolution of carbon atoms in the bulk of the catalyst particles is accompanied by the formation of a bulk metal carbide [41,42]. Conversely, some authors [43–47] supposed that decomposition of carbon-containing precursors is accompanied by dissolution of carbon without the formation of carbide. An *in situ* XRD study revealed an increase in the nickel lattice parameters upon decomposition of methane [46], which indicates the insertion of carbon into the metal without the formation of a nickel carbide, whereas in Ref. [47] the structure of the metallic nickel did not change during the decomposition of C_2H_2OH . Such discrepancies may be related to differences in the process conditions and methods of investigation (*in situ* or *ex situ*). However, there is convincing evidence for the formation of surface metal carbide MeC_x during the growth of undoped CNMs from *in situ* microscopy and XPS experiments [13].

Information on the state of the catalyst bulk during the growth of N-CNMs is also contradictory. According to Ref. [29], bamboo-like N-MCNTs may be obtained on an iron catalyst *via* the pyrolysis of a 2% ferrocene solution in acetonitrile *via* the formation of iron carbide. In Ref. [27], a mechanism including carbon and nitrogen diffusion through catalyst particles was proposed for the formation of similar bamboo-like tubes by decomposition of melamine on an iron catalyst. However, when studying the pyrolysis of melamine on nickel, the same authors supposed that only carbon is dissolved in the catalyst particle, while nitrogen diffuses over the surface.

In the present work, we have studied the formation of CNFs and N-CNFs on nickel-containing catalysts to compare the growth mechanisms of these materials. In the case of CNF growth on the nickel catalyst used here, a nickel carbide microphase forms on the surface of the nickel particles at 400–500 °C, as shown schematically in Fig. 10(a).

The size of the indicated microphase is dependent on the CNF growth conditions. If the temperature is increased and the reaction is performed with hydrocarbons that are less actively carbonized, the microphase transforms into surface carbide-like intermediates on the metal surface. Decomposition of the carbide-like compounds yields a system with a substantial oversaturation of the metal surface with carbon (C_{surf}) – two orders of magnitude greater than the concentration of saturated carbon solution in the bulk of the metal (C_{bulk}). Indeed, decomposition of such compounds produces a mixture with an atomic ratio Ni/C that may be close to the composition Ni_3C

Fig. 10. Schematic representation of the growth mechanism of CNFs on the Ni catalyst (a) and N-CNFs on the Ni-Cu catalyst (b) and the TEM images of the resulting CNFs and N-CNFs.

($C_{surf} \approx 0.5 \text{ g/cm}^3$). The concentration of saturated carbon solution in the bulk of the nickel was $C_{bulk} = 3.8 \times 10^{-3} \text{ g/cm}^3$ [35] at 600 °C. The proposed model was validated by calculating the rate of CNF growth.

It is known that carbon precipitates on metallic nickel as CNFs. The metallic particles reside on the tips of the nanofibers and serve as the catalyst for hydrocarbon decomposition. An oversaturation of carbon forms at the surface of the metallic particles. The nanofibers grow continuously as a result of the diffusion of carbon atoms through the bulk of the metallic particles. The diameter of each nanofiber is approximately equal to the diameter of the greatest cross-section of its metallic particle. The rate of nanofiber growth can be calculated under the assumption that it should be equal to the minimum rate of carbon diffusion through the bulk of the metallic particle. As determined from electron microscopy images, the maximum diffusion length l is close to the diameter of the metallic particle.

The amount of carbon (Q) diffusing through a unit cross-section area of metallic nanoparticle per unit time is determined by the equation:

$$Q = D\Delta C/l = D(C_{surf} - C_{bulk})/l$$

where D is the coefficient of carbon diffusion through nickel ($3.89 \times 10^{-10} \text{ cm}^2/\text{s}$), and ΔC is the concentration gradient of carbon along the particle length l .

Then, the linear rate of nanofiber growth V may be determined by the relation:

$$V = Q/d_c = D(C_{surf} - C_{bulk})/d_c l$$

where d_c is the density of carbon, equal to 2 g/cm^3 [35].

The calculated value of V for CNF growth on a Ni catalyst

particle with $l = 60$ nm upon decomposition of 1,3-butadiene at $600\text{ }^{\circ}\text{C}$ was 1.65×10^2 nm/s, which agrees well with the known experimental values of $0.8 \times 10^2 - 1.6 \times 10^2$ nm/s [35].

In the case of N-CNFs, it is commonly accepted that the mechanism of their growth on metal catalysts is similar to that of undoped carbon materials [26–28]. However, direct experimental data in favor of this hypothesis are virtually missing. In our work, the use of *in situ* XRD analysis supplemented with XPS data made it possible to demonstrate that the growth of N-CNFs on Ni-Cu catalyst is accompanied by the formation of non-stoichiometric nickel carbide on the catalyst surface and dissolution of carbon in the bulk of the catalyst. The lattice parameter values obtained for $\text{Ni}_{0.85}\text{Cu}_{0.15}$ alloy during N-CNF growth were used to calculate the average concentration of carbon in the bulk of the catalyst particles, which was equal to ~ 2 at.% [40]. However, the existence of a considerable carbon concentration gradient along the length of the metallic particles should be taken into account. Thus, the concentration of carbon in the subsurface layer of nickel particles in contact with the reaction medium should be much higher than 2 at.%. Analysis of N-CNF growth on Ni-Cu catalyst from pure ethylene or ethylene diluted with ammonia resulted in the conclusion that nitrogen also dissolves in the bulk of the particle, as shown in Fig. 10(b). This conclusion can be derived from the correlation between the lattice parameter of Ni-enriched alloy in the reaction, the composition of the $\text{C}_2\text{H}_4/\text{NH}_3$ reaction mixture, and the amount of nitrogen in the obtained N-CNFs: the increase in the lattice parameters of the $\text{Ni}_{0.85}\text{Cu}_{0.15}$ alloy during reaction with $\text{C}_2\text{H}_4/\text{NH}_3$ mixture was greater than for the case with pure ethylene. This is because the atomic radius of nitrogen is greater than that of carbon. Thus, the diffusion of nitrogen atoms also proceeds alongside the diffusion of carbon atoms.

Decomposition of $\text{C}_2\text{H}_4/\text{NH}_3$ mixture on nickel catalysts leads to the formation of a cubic phase with the mixed composition NiC_xN_y . The formation of such a phase may be the reason for the low activity of this catalyst during N-CNF growth. The presence of copper in the Ni-Cu catalyst prevents the formation of a NiC_xN_y cubic phase, explaining its higher activity than that of the Ni catalyst [34].

4. Conclusions

Experimental comparison of the growth mechanisms of CNFs on Ni and N-CNFs on Ni-Cu and Ni catalysts has shown that both processes occur by a mechanism that includes the formation of surface non-stoichiometric nickel carbide followed by the dissolution and diffusion of carbon or carbon and nitrogen through the bulk of the catalyst particle.

Acknowledgment

The study was financially supported by the Russian Science Foundation (Project No. 15-13-10043).

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Graphical Abstract

Chin. J. Catal., 2016, 37: 169–176 doi: 10.1016/S1872-2067(15)60982-2

Comparison of growth mechanisms of undoped and nitrogen-doped carbon nanofibers on nickel-containing catalysts

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A similarity of the growth mechanisms of carbon nanofibers and nitrogen-doped carbon nanofibers on Ni-containing catalysts was demonstrated by the use of XPS and XRD in situ techniques.

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Ni基催化剂上未掺杂和氮掺杂的碳纳米纤维生长机理的比较

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摘要: 研究了Ni催化剂上碳纳米纤维, 以及Ni和Ni-Cu催化剂上N掺杂的碳纳米纤维的生长机理。结果表明, 这两个过程的机理均包含了表面非计量碳化镍的形成, 然后是碳或碳和氮通过催化剂颗粒体相的溶解和扩散。

关键词: 碳纳米纤维; 氮掺杂; 生长机理; 镍基催化剂

收稿日期: 2015-08-28. 接受日期: 2015-09-30. 出版日期: 2016-01-05.

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